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Characteristic features of heterophase macromolecular chain reactions involving antioxidants in a non-crystalline polymer matrix

Yu A Mikheev, L N Guseva, G E Zaikov

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Abstract. The principles of kinetic modelling of free-radical chain processes initiated in an amorphous polymer matrix are presented. The chemical modelling was based on a micellar-sponge model of the supermolecular structure, which takes into account the behaviour of the heterogeneous zones, differing in size and fluctuational dynamics of micropores forming these zones. The influence of antioxidants on chain processes is associated with the existence of conjugated reaction chains localised in various zones of chain-sponge micelles. Considerable attention is paid to the mechanism of autooxidation of polyalkenes, containing sterically hindered alkylphenols, during the induction period. The induction period preceding the oxidation of a polymer is considered as a stage involving chain co-oxidation of the antioxidant and the polymer, which follows zero- or first-order kinetics with respect to the antioxidant (alkylphenol) depending on its molecular structure. The bibliography includes 54 references.

I. Introduction

According to the morphological model of a noncrystalline polymer, developed recently,^{1–9} an amorphous polymer consists of globules occurring in close contact with one another and incorporating large numbers of sponge-like polymer chains. An intraglobule chain-sponge micelle is considered as a chemical reactor. Two types of structural zones are distinguished within a micelle. In these zones, chain units experience unequal mechanical tension; they are confined by micropores, the real traps for reactive species, which have different sizes and are characterised by different fluctuation dynamics. Consequently, non-equivalent conditions

for the excitation of generation, propagation and termination of reaction chains are developed in different zones.

The closest packing of polymer chains cannot be achieved inside the globules; the degree of their loosening remains higher than that in a θ -solvent. This is due to the fact that globules in a block polymer are joined through their shells, the latter forming a continuous spatial p-framework.^{1,2,6,8} Paracrystalline domains of this p-framework, formed from small sections of chain units, act as mechanical clamps preventing the main regions of the polymer chains inside the globules from assuming a conformation of statistical knots characterised by maximum close packing.

The combination of spatial stretching fixed by the p-framework with the flexibility of polymer chains predetermines many features distinguishing amorphous polymers from homogeneous liquids. For example, there exist indirect methods that make glassy polymers compatible with low-molecular-weight compounds, although they are not mixed spontaneously upon direct contact.⁷ Many initiators and inhibitors of chain processes, used practically, which are sufficiently volatile and have access to the inner surfaces of structural cavities in a glassy polymer can be absorbed in it but only in minor amounts. However, larger amounts of the same compounds can often be introduced into the polymer from their joint solution in a common solvent at the stage of solvent evaporation.⁷

It is known that solvent molecules can exchange places, more or less easily, with chain segments, which ensures high entropy of mixing, and an intraglobule sponge micelle is thus converted into a liquid drop of a joint solution.⁹ A non-solvent molecule of a foreign admixture, which occupies in a chain sponge the site formerly belonging to a solvent molecule, is forced to push the polymer chain units apart, thus preventing them from packing more closely and, to some extent, ordering them with respect to itself. Consequently, a non-solvent molecule introduced into the sponge forms a micropore to 'match' its size, which is larger than the micropore existing without the admixture, and thus creates room for itself. The crowded sponge is compressed and, pressing against the paracrystalline globule shell, it in turn exerts an influence on the admixture through the surface forces of the micropore walls, which encapsulate the admixture molecule. Since the elastic forces of the sponge and the dispersion forces of interaction of the micropore surface with the admixed molecule

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are balanced with one another, the admixed molecule is localised within the pore and thus has more freedom to rotate.

Polymer chains that have no opportunity to form close packing within a sponge micellar structure but tend to reach the highest cohesion density, create zones containing micropores with different sizes. In the absence of admixtures, a grain is formed inside a globule bound in a framework; the grain contains narrow micropores with sizes of up to 0.5 nm, which corresponds in order of magnitude to the thickness of the polymer chain.

Such a grain (called v-zone) is separated from the walls of the p-framework cell (*i.e.* from the shell of the globule) by a spherical layer of stretched chain segments oriented in radial directions in the globule. These segments act as mechanical tension wires and fix a layer of stationary super-s-micropores, the sizes of which are close to the length of a thermodynamic segment (1.5–3.0 nm).

The presence of separate microporous zones within the p-framework cells accounts for the heterogeneous distribution of molecules of admixtures (for example, initiators, inhibitors, oxygen, etc.). The greater part of an admixture is accumulated in the internal v-grains, because the energy of sorption in the narrow v-micropores of these grains is larger than that in the ample s-micropores. As has already been noted, upon capturing an admixture, the narrow v-micropores are forced to become larger, which ensures a fairly high frequency of rotation of admixed particles. The frequency of steps of migration of the admixed particles along the micropore system also increases. This is because thermal fluctuation pulsations of the sponge v-grains hanging on the walls of the p-framework stimulate the cooperative vibrations of the chain segments of the sponge. Owing to these fluctuations, a probability appears, although only for a short period, that the size of the narrow v-micropores will increase up to that of the s-micropores. Consequently, relatively small admixture particles become fairly free to move within the sponge, which enhances exchange between the v- and s-zones.

The functioning of stationary s-micropores and fluctuation-labile v-micropores in sponge micelles has an effect on the mechanism of initiated transformations, because molecules of an initiator migrate between the s- and v-zones thus changing their steric and energy states. Consequently, their initiating ability in these two zones would be different. In fact, in narrow v-micropores, the force fields of the opposite walls overlap. Under these conditions, the initiator molecule is pushed to the bulk of the pore and is mostly located there, executing only short-term fluctuation-activated jumps. Owing to the short duration of these jumps, even if a primary radical pair arises upon occasional decomposition of the initiator molecule in the v-zone, the radicals of this pair cannot move far from each other.

To the contrary, in ample s-micropores, conditions for the dissociation of initiator molecules are much more favourable than those in narrow v-micropores. This is due not only to the presence of free space but also to the fact that the force fields of the opposite walls do not overlap and, consequently, an admixed particle spends most of the time on the pore surface as an adsorbed species rather than within the pore bulk. Under these conditions, the radicals of a radical pair formed spontaneously do not experience compression forces any longer; instead, under the action of adsorption forces, they efficiently attack polymeric molecules.

The presence of dissimilar zones also influences the fate of the polymeric radicals, which are able to decompose with rupture of the chains. It is clear that the probability of this event occurring on the surface of a compressed v-micropore is low, since this requires that a series of segments ensuring the fixing of the v-micropore walls would shift synchronously, which is possible only if the fluctuation mobility of the chain-sponge grains is very high.

At the same time, on the surface of s-micropores, the probability for the degradation of polymer radicals accompanied by chain rupture is substantially higher. This is due to the presence of free space and to mechanical stretching of the s-segments of polymer chains.

The above characteristic features of the heterogeneous structure of chain-sponge micelles constituting the matrix of a non-crystalline polymer make the problem of kinetic description of a chain process more complicated than that of a homogeneous reaction. To construct an adequate mechanism for a polymer transformation, one must take into account the heterogeneity of the system and abandon the simplified representation of the reaction medium as a structureless liquid-phase system. This resembles the situation, which arose at one time in the field of heterogeneous catalysis;¹⁰ therefore, the current problem could also be solved by design and selection of structural-kinetic models for reactions.

The modelling of chain transformations of polymers has been started with consideration of a model chain reaction of dibenzoyl peroxide (BP) with polymers of various structures (cellulose triacetate, polycarbonate, polystyrene and polyamide PA-548).^{3,9,11–13} Later, chain decomposition of polymeric peroxides has been modelled.^{5,6}

According to the views of that time on a heterogeneous reaction, a complete representation of a transformation should include: (1) a scheme for the primary reaction chains, which propagate in the ample micropores of s-zones of sponge micelles; (2) a scheme for the secondary reaction chains, which occur in the narrow micropores of v-zones; and (3) a scheme for the transfer of free radicals between the zones.

It may be expected that peculiar features of the supermolecular organisation of polymer chains will also influence the transformations of antioxidants used to stabilise polymeric materials during their processing and operation. Antioxidants have been widely employed in polymers since the polymers themselves came into universal use; however, up to now, the development of scientific views about the mechanism of their protective effect has remained within the framework of theories of homogeneous reactions.^{14–16} At the same time, the study of model chain reactions of dibenzoyl peroxide with polymers made it possible to discover significant specific features of the influence of phenolic antioxidants on this process resulting from microheterogeneity of the polymer matrix.^{17,18} In this review, we report briefly these results and analyse some important published data on the mechanism of the action of antioxidants, which have not yet been adequately explained. A structural-kinetic reaction model is developed, which discloses the physical essence of the action of antioxidants in a real heterogeneous process, polymer ageing. This model necessitates complete revision of the attitude towards the postulates, transferred from the theory of homogeneous reactions to the chemistry of polymers.

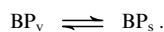
II. The mechanism of the influence of 2,6-di-*tert*-butyl-4-methylphenol on the anaerobic chain reaction of dibenzoyl peroxide with glassy cellulose triacetate and polycarbonate

1. Regularities of a model reaction

Studies of the reaction of BP with cellulose triacetate (CTA) and polycarbonate (PC)^{2,11} included measurements of the kinetics of consumption of BP ($T \leq 371$ K) and of accumulation of benzoic acid and phenyl benzoate and determination of the numbers of ruptured polymeric bonds and decomposition fragments of BP grafted to polymer chains.

Spontaneous decomposition of BP was found to occur in those structural zones of the polymer matrix in which macroradicals do not induce decomposition of BP and the related addition of the peroxide fragments to the polymer. The effective rate constant k_0 for the spontaneous decomposition of CTA or PC at 371 K is $4.8 \times 10^{-3} \text{ min}^{-1}$ (the activation energy $E_0 = 117 \text{ kJ mol}^{-1}$). The rate constant is described by the expression $k_0 = k_{0s} K_e m_s m_v^{-1}$, where m_s and m_v are masses of the s- and v-zones, respectively, k_{0s} is the rate constant for decomposition of

BP in s-micropores, and K_e is the equilibrium constant for the interzone distribution



The condition of equilibrium for the BP exchange between the zones has the following form:

$$c_s = K_e c_v \approx \frac{K_e c}{\alpha}, \quad (1)$$

where c_s , c_v and c are the concentrations of BP in s-zones, in v-zones, and in the whole sample, respectively; α is the mass fraction of sponge micelles consisting of both types of zones. This equilibrium, which ensures heterogeneous generation of radicals from the very beginning of the process, is not disturbed during the decomposition of BP, the rate of which is much lower than the rate of the interzone exchange.

Spontaneous decomposition of BP gives molecular products in high yields. These are phenyl benzoate and products resulting from the addition of radicals derived from BP to the benzene rings of PC. Benzoic acid and macroradicals with free valences located either in side groups ($R_s^\bullet$) or in the backbone ($P_s^\bullet$) are formed in a lower yield (the effective rate constant is $0.2k_0$). Decomposition of the latter is accompanied by chain rupture and by a decrease in the molecular weight of the polymer.

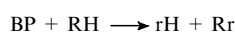
The terminal radicals arising upon destruction of the chain as well as the $R_s^\bullet$ radicals undergo transformations, which lead ultimately to the elimination of the free valence without formation of cross-linking bonds between the polymer chains.

The rate of accumulation of ruptured polymer chains and the variation of the concentration of breaks (n) with time during the processes involving CTA and PC are expressed by identical relations:

$$\begin{aligned} \frac{dn}{dt} &= k_n c_0 \exp(-kt); \\ n &= n_\infty [1 - \exp(-kt)]. \end{aligned} \quad (2)$$

Here, c_0 is the initial concentration of BP in the sample; k is the effective rate constant for decomposition of BP; n_∞ is the limiting concentration of the ruptured chains; the k_n constant at 371 K is $0.062k_0$ and $0.14k_0$ for processes involving CTA and PC, respectively (if the polymer contains dissolved oxygen, k_n halves, due to the oxidation of radicals $R_s^\bullet$ yielding new radicals that react with the initial benzoyloxyl radicals);

Transformations of polymer chains in the v-zones differ from those in the zones of radical generation. They do not degrade but instead, they enter into a chain reaction with BP according to a simple stoichiometric ratio



(here, the symbol r refers to a benzoyloxyl radical).

The overall process of decomposition of BP in sponge micelle zones is described by an exponential equation

$$c = c_0 \exp(-kt), \quad (3)$$

and the overall effective rate constant consists of the non-chain and chain components:

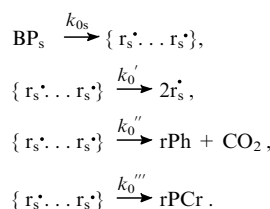
$$k = k_0 + k_c k_0 c_0.$$

The coefficients k_c in the chain component are similar for the reactions involving CTA and PC, unlike the situation occurring in liquid-phase systems: the rate of decomposition of BP in aromatic liquids is lower than that in non-aromatic liquids.

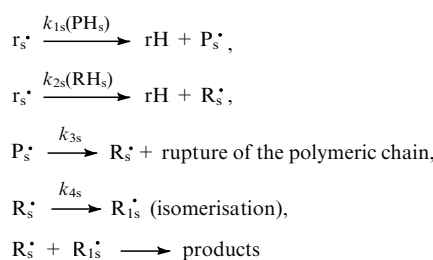
It has been found^{2,11} that the same reagents (BP molecules, polymer chain units, free benzoyloxyl radicals and macroradicals) exhibit different chemical properties in different structural zones. Three block schemes are used to describe the overall picture of

transformations occurring in polymers in the absence of dissolved oxygen.

The s-scheme describes generation of radicals and their subsequent transformations in zones of s-micropores. The process starts with the steps of formation of primary radical pairs:

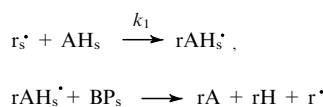


The liberated primary benzoyloxyl radicals undergo further transformations:



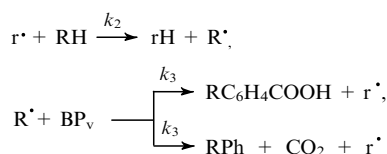
(here, the symbols $P_s^\bullet$ and $R_s^\bullet$ refer to radicals with the free valence in the backbone and in the side groups, respectively).

The transfer of radicals from the s-zone to the v-zone in the absence of oxygen in the samples is described by the tr-scheme:

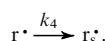


(here, the symbol A denotes the phenyl group of both the initial BP and the benzoic acid and phenyl benzoate formed). This scheme characterises the sequence of events occurring at a favourable arrangement of the species participating in this reaction bridge and surrounded by rigidly fixed chain segments, which confine s-micropores.

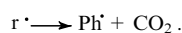
As a result of this s,v-transfer, the probability of which is low and which has no influence on the steady-state concentrations of s-radicals, secondary benzoyloxyl radicals $r^\bullet$ responsible for chain arylation of macromolecules appear in v-zones. The corresponding v-scheme has the following form:



(indices at the reagents are omitted, except for BP_v , the symbol $R^\bullet$ corresponds to a radical with the free valence at a side-chain group, $-\text{CH}_2^\bullet$). These reaction v-chains are terminated *via* the departure of mobile benzoyloxyl radicals to s-zones):



This v-scheme does not take into account the differences between the chemical structures of non-aromatic CTA and aromatic PC, which is consistent with experimental results; it does not also include steps of interaction of the aromatic rings of PC with light radicals and steps of decomposition



Whereas the $r_s^{\cdot}$ radical can add to the rings of PC in s-zones, this is apparently impossible in v-zones, because the rings in the v-framework cannot undergo conformational changes needed for the addition to proceed at intermediate stages.

The fact that decarboxylation of benzoyloxyl radicals in v-zones is absent for both polymers implies that one molecule of benzoic acid is formed in each unit of the chain decomposition of BP. This differs completely from the observations made for the reactions carried out in liquids in which the probability of decarboxylation of benzoyloxyl radicals is close to 100%. This distinction can be explained by the fact that rigid monomeric units in CTA and PC are fairly large and the volume of v-micropores is relatively small; consequently, the $r^{\cdot}$ radicals spend a lot of time on the rigid walls of the v-framework and thus have a good chance of abstracting hydrogen atoms from the alkyl substituents of macromolecules.

It should be noted that chain arylation of polymers decreases the total number of free phenyl groups, but this does not change the efficiency of the s, v-transfer involving them. This is due to the fact that the loss of a binuclear BP molecule is accompanied by the formation of a mononuclear benzoic acid molecule, which migrates along the system of micropores twice as fast as the molecule of BP. Hence, the probability of the interzone transfer of free valence is retained.^{2, 9, 11}

The non-equivalent reactivity of the same species in s- and v-zones, reflected in the above schemes, can be expressed in terms of the corresponding kinetic equations.

For example, the local rate of decomposition of BP in s-zones is described by the following equation

$$-\frac{dc_s}{dt} = k_{0s} c_s = \frac{k_{0s} K_e c}{\alpha}, \quad (4)$$

while that in v-zones is described by another equation

$$-\frac{dc_v}{dt} = k_3 [R^{\cdot}] c_v = k_2 [r^{\cdot}] [RH].$$

The concentration of benzoyloxyl radicals $[r^{\cdot}]$ can be found from the condition of equal rates of generation and termination of the reaction v-chains⁹

$$V_{tr} = k_4 [r^{\cdot}],$$

where

$$V_{tr} = k_1 [r_s^{\cdot}] [PhH_s] = 2\varphi k_1 \frac{[PhH_s] k_{0s} c_s}{k_{1s} [PH_s]} \quad (\text{Ref. 9}),$$

$$\varphi = \frac{k_0'}{k_0' + k_0'' + k_0'''},$$

$$[PhH_s] = 2 \frac{K_e c_0}{\alpha}.$$

After the necessary substitutions, we obtain

$$\begin{aligned} -\frac{dc_v}{dt} &= k_2 [r^{\cdot}] [RH] = \frac{k_2 [RH] V_{tr}}{k_4} = \\ &= 4\varphi \frac{k_2 [RH] k_1 K_e \alpha^{-1} c_0 (k_{0s} K_e \alpha^{-1}) c}{k_4 k_{1s} [PH_s]}. \end{aligned} \quad (5)$$

Now we pass from the local specific reaction rates in s- and v-zones to the overall reaction rate in the sample on the whole. This is calculated from the formula

$$-\frac{dc}{dt} = -\frac{m_s}{m} \frac{dc_s}{dt} - \frac{m_v}{m} \frac{dc_v}{dt}$$

where m_s , m_v and m are masses of s-zones, v-zones, and the whole sample, respectively. Taking into account the relation

$$\alpha = \frac{m_s + m_v}{m} \approx \frac{m_v}{m}$$

and Eqns (4) and (5), we obtain the following expression for the overall rate of the decomposition of BP

$$-\frac{dc}{dt} = k_0 c + k_c k_0 c_0 c = (k_0 + k_c k_0 c_0) c. \quad (6)$$

The rate of destruction, which occurs only in s-zones according to the s-scheme, is equal to

$$\begin{aligned} \frac{dn}{dt} &= k_{3s} [P_s^{\cdot}] = k_{1s} [r_s^{\cdot}] [PH_s] = 2\varphi k_{0s} c_s = \\ &= \frac{2\varphi K_e k_{0s} c}{\alpha} = \frac{2\varphi m k_0 c}{m_s} = k_n c. \end{aligned} \quad (7)$$

Both theoretical expressions, (6) and (7), are fully consistent with empirical formulae (2) and (3) and disclose the physical essence of heterophase transformations of units of polymeric-chain sponge in the inhomogeneous structural zones.

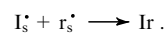
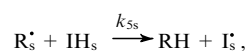
The heterophase scheme under consideration can be used equally well to explain the kinetic regularities of the formation of products of non-chain and chain reactions such as phenyl benzoate, benzoic acid and arylated macromolecules.

2. Characteristic features of the model anaerobic reaction in the presence of ionol

The non-equivalence of transformations of reagents in different structural zones of sponge micelles is also retained when ionol (2,6-di-*tert*-butyl-4-methylphenol, IH) is present as an admixture. The influence of this substance on model reactions of BP with polymers has been studied.^{17, 18}

Ionol itself influences the processes occurring in s- and v-zones in different ways. For example, ionol present in a relatively low concentration, $c_i \approx 0.05 \text{ mol kg}^{-1}$, causes virtually complete termination of chain arylation of polymers, whereas the process of initiated destruction is only slightly decelerated even at very high c_i . In the case of PC, as c_i varies from 0.023 to 0.64 mol kg^{-1} , the rate constant for destruction (k_n) decreases only by one half and then remains constant.

In terms of the theoretical model for a heterophase reaction, this is explained by the two-fold decrease in concentration of primary benzoyloxyl radicals $r_s^{\cdot}$ due to their interaction with the phenoxyl radicals arising *via* the reaction of ionol with side-chain and terminal macroradicals $R_s^{\cdot}$.



Thus, expression (7) for the rate of destruction assumes the form

$$\frac{dn}{dt} = 0.5 k_n c. \quad (8)$$

The fact that the rate constant for destruction (k_n) decreases in the presence of ionol by only 50% indicates that the efficiency of direct interaction of ionol with primary benzoyloxyl radicals in a PC matrix is extremely low. Apparently, the spatial arrangement of these reagents adsorbed on the walls of s-micropores is unfavourable for the reaction.

Figure 1 presents the results obtained by analysis of the decomposition of dibenzoyl peroxide in PC in terms of the heterophase scheme. The character of the curves describing the accumulation of ruptured polymer bonds (2–4) indicates that the limiting concentrations of the ruptured bonds decrease upon an increase in c_i , because BP is consumed in another reaction, the mechanism of which will be considered below. Here we only

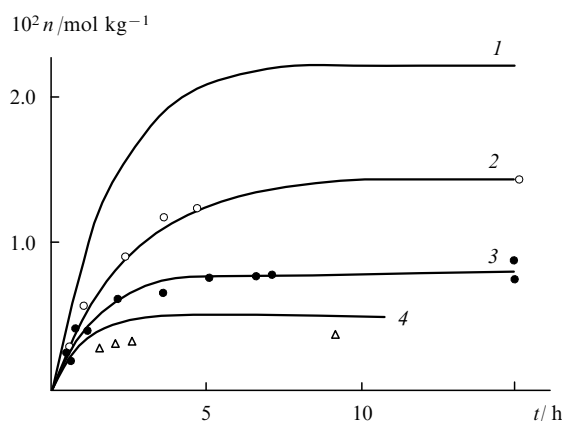
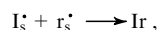
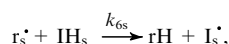


Figure 1. Accumulation of broken polymeric chains during decomposition of 0.29 mol kg^{-1} of dibenzoyl peroxide at 371 K in evacuated polycarbonate films containing ionol in concentrations, $c_i / \text{mol kg}^{-1}$: 0 (1); 0.023 (2); 0.32 (3); 0.64 (4). Curves (1–4) were obtained by calculations, and the points show the experimental results.

mention that according to Eqn (8), the initial rate of the destruction, which can be found from the initial sections of curves 2–4, decreases by only one half with respect to the initial rate of the destruction of PC in the absence of ionol (Fig. 1, curve 1).

Some deviation of the calculated curve 4 from the experimental points is due to the fact that for very high c_i values, the contribution of the direct reaction between ionol and primary benzyloxy radicals



which is not taken into account, becomes noticeable. In the reaction involving CTA, this contribution is greater; however, in this case too, destruction is not terminated completely even at a high concentration of ionol, $c_i = 0.32 \text{ mol kg}^{-1}$.

In the v-zones of chain-sponge micelles, in which decomposition of BP induced by macroradicals is inhibited even at low c_i , ionol reacts with benzyloxy radicals in a completely different way. This is manifested both in a decrease in the effective rate constant (k_i) for the consumption of BP and in the fact that the synthesis of arylated macromolecules ceases.

The overall process of BP decomposition in the presence of ionol obeys an exponential kinetic law

$$c = c_0 \exp(-k_i t), \quad (9)$$

According to this equation, the k_i constant, which characterises this reaction at any degree of conversion, depends on the initial concentrations of BP (c_0) and ionol (c_{i0}). To illustrate this, several $c(t)$ dependences plotted in semilogarithmic coordinates and referring to the decomposition of BP in CTA films, are presented in Fig. 2.

It can be seen from Fig. 2 that the smallest k_i value is achieved in those samples, which have been heated in air (curve 1); in this case, k_i coincides with the constant k_0 for spontaneous decomposition of BP. For c_0 and c_{i0} ranging over the same limits but in the absence of oxygen, k_i varies in a complex manner: at low c_0 (0.02 mol kg^{-1}), it increases proportionally to c_i (Fig. 3, straight line 1), whereas at high c_0 , it sharply diminishes as c_i increases, reaches a minimum at $c_i = 0.05 \text{ mol kg}^{-1}$, and then increases again (Fig. 3, curves 2, 3 and 5).

In the presence of ionol, a catalytic branch of BP decomposition appears (Fig. 3) in which the rate of chain decomposition under the action of macroradicals is negligibly small. Firstly, this is indicated by straight line 1 in Fig. 3: in this case, chain arylation

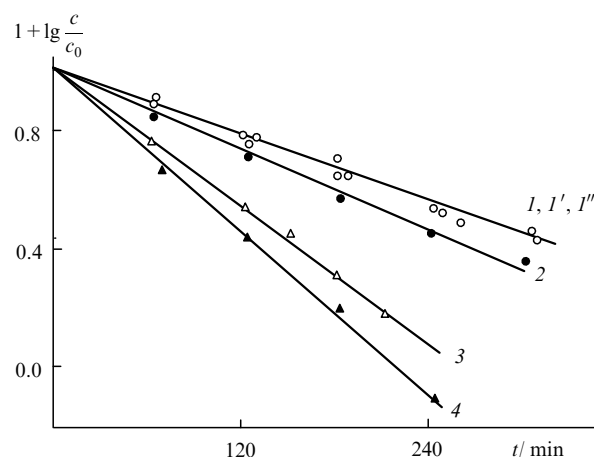


Figure 2. Semilogarithmic plots for the curves for consumption of dibenzoyl peroxide at 371 K in aerated (1) and evacuated (2–4) cellulose triacetate films containing BP and ionol in concentrations, mol kg^{-1} : for (1), (1'), and (1'') — $c_0 = 0.02, 0.25$, and 0.63 , $c_{i0} = 0.08, 0.10$, and 0.11 , respectively; (2) — $c_0 = 0.02$, $c_{i0} = 0.027$; (3) — $c_0 = 0.66$, $c_{i0} = 0.042$; (4) — $c_0 = 0.02$, $c_{i0} = 0.27$.

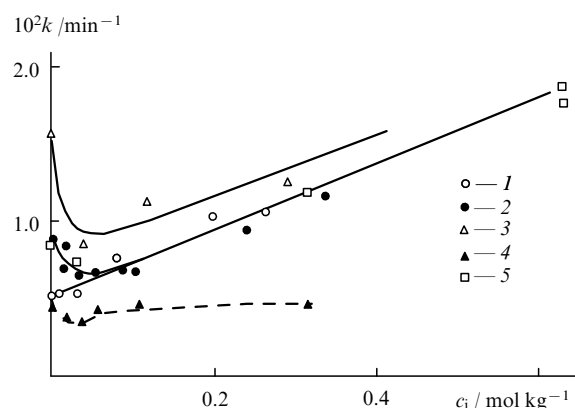


Figure 3. Dependence of the effective rate constant for the decomposition of BP at 371 K on the concentration of ionol in evacuated (1–3, 5) and aerated (4) CTA (1–4) and PC (5) films containing BP in the following initial concentrations mol kg^{-1} : 0.02 (1); 0.27 (2, 4, 5); 0.64 (3).

does not make significant contribution to the decomposition of BP even when no ionol is present, because c_0 is fairly low. Secondly, this is confirmed by the fact that the accumulation of arylation products, which is followed using the UV spectra of CTA, almost ceases after BP has wholly decomposed (in the range of c_0 from 0.15 to 0.7 mol kg^{-1}) and the decomposition products have been extracted with methanol (Fig. 4). The straight line 1 in Fig. 4 corresponds to chain grafting of BP fragments to CTA in the absence of ionol, and curve 2 corresponds to the same process in the presence of ionol ($c_{i0} = 0.22 \text{ mol kg}^{-1}$). Curve 3 was constructed using measurements of the optical density at $\lambda = 333 \text{ nm}$, which is beyond the absorption spectrum of grafted BP fragments, while curves 1 and 2 were obtained by measuring the optical density at the maximum of the absorption band of these fragments ($\lambda = 284 \text{ nm}$). Complete correlation between curves 2 and 3 indicates that the formation of a minor amount of UV-absorbing products in this case is associated with grafting of only a small number of ionol groups and not of BP fragments to the polymer.

Speaking again about the reasons for the appearance of catalytic branches in the curves in Fig. 3, it should be mentioned that they refer to decomposition of BP caused by free radicals derived from ionol rather than by ionol molecules. This is why the

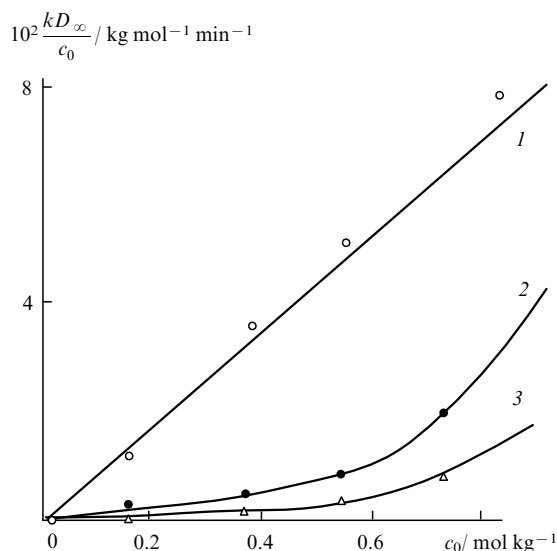


Figure 4. Dependence of the normalised optical density D_{∞} of arylated CTA on the concentration of BP without antioxidant (1) and in the presence of 0.22 mol kg^{-1} of ionol (2, 3). The D_{∞} values were measured at an UV radiation wavelength of 284 (1, 2) and 333 (3) nm for solutions of films in dichloromethane, after anaerobic decomposition of BP at 371 K and extraction of low-molecular-weight compounds from the films with methanol.

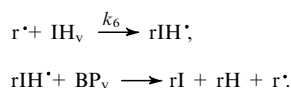
catalytic effect disappears completely when the polymer films contain dissolved air; the rate of decomposition of BP in aerated films is equal to the rate of its spontaneous decomposition (straight line 1 in Fig. 2 and curve 4 in Fig. 3).

Free phenoxyl cannot act as a radical carrying new chains of BP decomposition, since it ensures linear termination of chains of arylation of macromolecules. In addition, it is known that phenoxyl radicals derived from sterically hindered phenols (including ionol) are not oxidised by oxygen and dibenzoyl peroxide at 371 K.^{19–21}

The σ -complex formed upon addition of benzoyloxy to the benzene ring of ionol acts as a new initiator of the chain decomposition of BP. The formation of σ -complexes in reactions of ionol with alkyl macroradicals can be neglected, because the data presented in Fig. 4 indicate that the rate of this addition is low even at high concentrations of ionol ($c_i = 0.22 \text{ mol kg}^{-1}$).

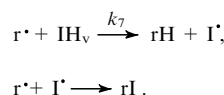
In solutions, ionol and other sterically hindered phenols also do not add alkyl radicals,¹⁶ and their σ -complexes with benzoyloxy radicals are extremely unstable; they rapidly dissociate into the initial species, $r^{\cdot}$ and IH , and exert no influence on the rate of decomposition of BP.^{9, 19} However, admixture species in v-zones of chain-sponge micelles, unlike those in liquids, experience the effect of the overlapping surface forces from the closely spaced walls of v-micropores; consequently, these species are localised within the bulk of the pores. This favours mutual contacts between the species and hampers their dissociation. Recall that a similar structural effect of the chain sponge accounts for the decrease in the rate of dissociation of BP in narrow micropores of v-zones. For a similar reason, the stability of the ionol σ -complexes and the probability of their interaction with BP molecules migrating in v-zones increase.

These transformations of ionol can be represented by the following scheme:



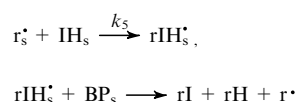
The termination of new reaction chains occurs both upon the migration of benzoyloxy radicals from v-zones to s-zones (with

rate constant k_4) and in processes involving the phenoxyl radicals formed



If we consider these reactions in terms of the above scheme for the decomposition of BP, it is not difficult to find out that they do not suffice to account for the increase in the constant k_i in the region of high c_{i0} values, since both the rate of the chain reaction (k_6) and the rate of chain termination (k_7) depend on c_i in the same manner.

The linear $k_i(c_i)$ dependence in the catalytic branches of the curves (see Fig. 3) indicates that an additional route for the injection of radicals from s-zones to v-zones, which involves ionol, should be considered:



Now, taking into account both routes of the s,v-transfer of free valence (involving PhH and ionol) and the fact that the rates of generation and termination of the reaction v-chains are equal, we obtain an expression for the concentration of benzoyloxy radicals in the v-zone:

$$[r^{\cdot}] = \frac{(k_1[\text{PhH}_s] + k_5 c_{is})[r_s^{\cdot}]}{k_4 + 2k_7 c_{iv}} \quad (10)$$

When the content of ionol (c_{i0} , c_{is} and c_{iv}) is relatively high, the concentration of $r^{\cdot}$ markedly decreases, and Eqn (10) is transformed into the following expression

$$[r^{\cdot}] = \frac{k_5 c_{is} [r_s^{\cdot}]}{2k_7 c_{iv}},$$

which actually implies that $[r^{\cdot}]$ does not depend on the concentration of ionol, because during the interzone exchange of ionol, the following equilibrium is established:

$$c_{is} = K_{ei} c_{iv} \approx \frac{K_{ei} c_{i0}}{\alpha},$$

(here K_{ei} is the constant of the corresponding equilibrium). Thus, Eqn (10) assumes the following form

$$[r^{\cdot}] = \text{const } k_0 c.$$

In conformity with the extended heterophase scheme, the rate of decomposition of BP in v-zones is the sum of two terms

$$-\frac{dc_v}{dt} = k_3 [R^{\cdot}] c_v + k_6 [r^{\cdot}] c_{iv} = k_2 [r^{\cdot}] [\text{RH}] + k_6 [r^{\cdot}] c_{iv} \quad (11)$$

The contribution of the first term is significant only at very high concentrations of dibenzoyl peroxide c_0 , because ionol decreases markedly the concentration of $r^{\cdot}$. Taking this into account, the overall rate of decomposition of BP in s- and v-zones can be approximated by the expression

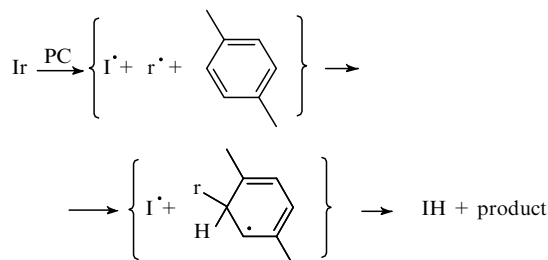
$$-\frac{dc}{dt} = k_0 c + k'_i c_{i0} c = (k_0 + k'_i c_{i0}) c = k_i c, \quad (12)$$

which characterises the catalytic branch of decomposition of BP associated with the influence of ionol.

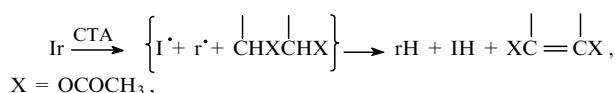
Here the following important circumstance should be recalled: the initial concentration of ionol c_{i0} appears in the expression for the effective rate constant k_i as a constant parameter at any ratios of c_{i0} and c_0 (Fig. 2, straight lines 2–4). The fact that the c_{i0} is virtually invariant has been confirmed by IR spectroscopic analysis of CTA and PC films, which indicates that the intensity of IR absorbance by phenolic OH groups decreases only slightly

during the reaction.^{17,18} This invariance of absorbance (which is also typical of the reaction of ionol with BP in a polystyrene matrix⁹) implies that a mechanism for the regeneration of ionol from the main product of the transformations, Ir, is accomplished in the polymers.

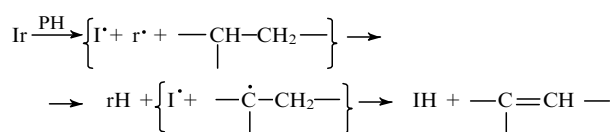
The compound Ir is unstable in solutions and dissociates quickly to give benzoyloxy and phenoxy radicals.¹⁹ Apparently, molecules of this compound also dissociate in a polymer-chain sponge matrix on the walls of the fluctuationally excited v-micropores, which have become as large as s-micropores for a short period. The free radicals thus formed cause dehydrogenation of the polymer by one or another mechanism, depending on the structure of macromolecules. In the case of PC, the corresponding process can be represented in the following way:



Dehydrogenation of CTA occurs by the following scheme:

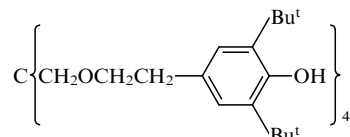


while the transformation in a carbocyclic polymer follows the scheme



The reactive species dehydrogenating the polymer should not leave their reaction cage, and the whole process, which occurs by a sort of 'latent radical' mechanism, should be accomplished over the life span of the excited state of the micropore.

The influence of other sterically hindered phenols studied by us, in particular, of the tetraphenol



and 2,4,6-tri-*tert*-butylphenol (at a relatively high concentration) on the decomposition of BP is qualitatively similar to that of ionol (Fig. 5, curves 2–4). However, their catalytic efficiency is much lower (when the concentration of BP is small, tri-*tert*-butylphenol does not accelerate its decomposition at all, curve 1), which is apparently due to the fact that the participation of these phenols in the steps in the interzone s, v-transfer of free valence is less probable. However, the results considered above clearly indicate that in the chain-micellar matrix of a polymer, the radicals with free valence on oxygen atoms add to the aromatic rings of the phenols, and the σ -complexes thus formed participate in subsequent transformations. Consequently, phenolic antioxidants act as carriers of the free valence between s- and v-zones and intrazone carriers of the reaction v-chains of the BP decomposition.

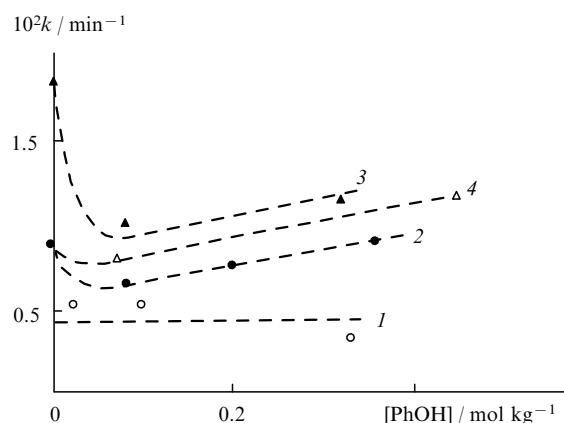


Figure 5. Dependence of the effective rate constant for the decomposition of BP at 371 K in evacuated CTA films on the concentration of 2,4,6-tri-*tert*-butylphenol (1–3) and on the concentration of phenolic groups of the tetraphenol 'Irganox-1010' (4) at c_0 / mol kg⁻¹: 0.023 (1); 0.2 (2, 4); 0.76 (3).

III. Specific features of the model reaction in the presence of bisphenol

In the presence of 2,2'-methylenebis(6-*tert*-butyl-4-methylphenol) or bisphenol 2246 (HIIH), the rate of anaerobic decomposition of BP in glassy CTA increases to even a greater degree.²² The curves describing the decomposition of BP in the presence of HIIH, plotted on semilogarithmic coordinates (Fig. 6), indicate that in this case, too, the process obeys an exponential law. However, unlike the situation with ionol, the apparent rate constant k_m for decomposition of BP in the presence of bisphenol increases in the catalytic stage proportionally to the squared concentration of the phenolic groups c_m ($c_m = 2[\text{HIIH}]$). The corresponding dependence of k_m on c_m^2 is shown in Fig. 7.

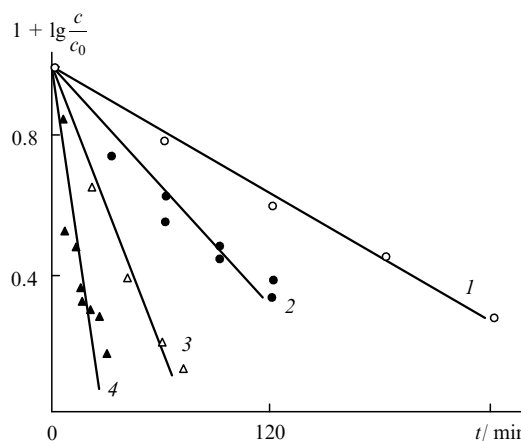


Figure 6. Influence of the concentration of phenol groups of 2,2'-bis(6-*tert*-butyl-4-methylphenol) on the transforms of the curves for decomposition of BP ($c_0 = 0.37$ mol kg⁻¹) at 371 K in evacuated CTA films. $2[\text{HIIH}]$ / mol kg⁻¹: 0.06 (1), 0.18 (2), 0.40 (3), 0.64 (4).

It can be seen that in the region of low c_m , this plot contains a very short section in which k_m decreases and a fairly extended catalytic branch. The first portion is due to the inhibition of the chain arylation of CTA; it was briefly considered in the previous Section. Here we shall discuss the mechanism of catalysis by bisphenol, the efficiency of which is much higher than that of catalysis by ionol and reaches a maximum value of

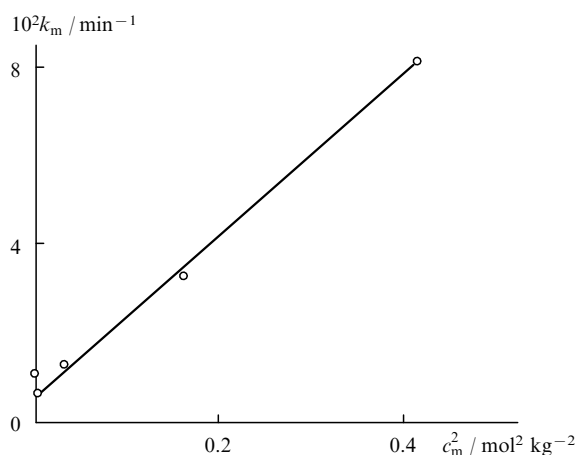


Figure 7. Influence of the concentration of the phenol groups of 2,2'-methylenebis(6-*tert*-butyl-4-methylphenol) on the effective rate constant for decomposition of BP at 371 K in evacuated CTA films at $c_0 = 0.37 \text{ mol kg}^{-1}$.

$$\frac{k - k_0}{k_0} = 16 - 17$$

at the highest concentration c_m studied. To begin with, we note that the empirical exponential law for the consumption of BP

$$c = c_0 \exp(-k_m t),$$

and the expressions for the effective rate constant

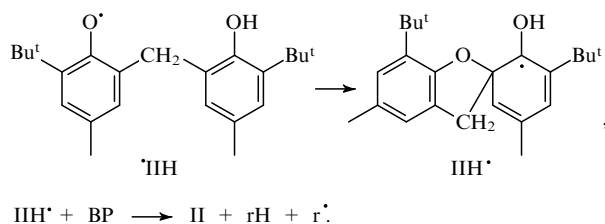
$$k_m = k_0 + k_c c_m^2$$

and for the reaction rate

$$-\frac{dc}{dt} = k_0 c + k_c c_m^2 c$$

make it possible to conclude that the chain constituent of the process obeys formally third order kinetics with respect to admixed reagents. At a high rate of the chain reaction, this alone indicates, irrespective of the mechanism of the process, that admixtures in the chain-sponge micelles of a glassy polymer are fairly mobile.

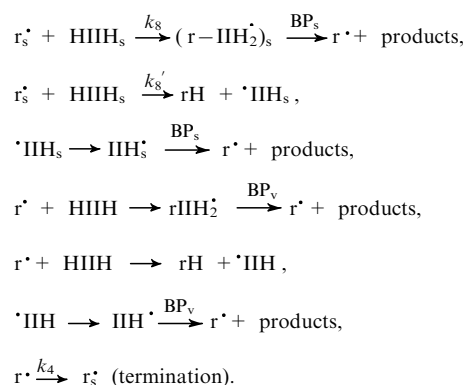
As regards the particular mechanism of the action of bisphenol 2246, it is natural to assume that its molecules, which actually consist of two ionol structures linked together, should enter into the same steps of s,v-transfer of radicals, induced decomposition of BP, and regeneration as does ionol. At the same time, the substantial enhancement of the catalytic effect and the change in the apparent order of the chain constituent of the reaction attest to an essentially different mechanism for the decomposition of BP in the presence of HIIH, which can be attributed to the specific mutual arrangement of the phenolic groups in the bisphenol molecule. This arrangement is quite favourable for the phenoxyl radical formed from bisphenol to isomerise into an intramolecular σ -complex, which, in its turn, is readily oxidised by dibenzoyl peroxide:



In view of this feature of bisphenol 2246, its specific influence on the model reaction can be explained by the fact that phenoxyl radicals and intramolecular σ -complexes derived from bisphenol do not participate in the termination of the reaction v-chains of decomposition of BP, and act as chain propagating species. Therefore, the transfer of v-benzoyloxyl radicals to s-zones occurring with the rate constant k_4 becomes the only route for the termination of the reaction v-chains.

Apparently, fast isomerisation of the phenoxyl radical into the σ -complex ($\text{IIH} \rightarrow \text{IIH}'$) also accounts for the fact that in solutions, the stoichiometric coefficient of inhibition by bisphenol 2246 and by other bisphenols containing analogous complementary phenolic groups is 2, as in the case of ionol, rather than 4, which might be expected with the assumption that the influences exerted by each phenolic group are additive.²³

With allowance for the above considerations, the following scheme can be proposed for generation, propagation, and termination of reaction v-chains:



According to this scheme, the concentration of v-benzoyloxyl radicals should be described by the expression

$$[\text{r}^*] = \frac{k_8 + k_8'}{k_4} c_{ms}.$$

If we substitute this relation in Eqn (11) and neglect the first term in this equation, which can be done because bisphenol 2246 is even a stronger acceptor of radicals than ionol,²³ we obtain the relation

$$-\frac{dc_v}{dt} = k_6 [\text{r}^*] c_{mv} = \frac{k_6 c_{mv} (k_8 + k_8') c_{ms}}{k_4}.$$

Taking into account the conditions for equilibrium in the exchange of bisphenol molecules ($c_{ms} = K_{em} c_{mv}$) and BP (Eqn 1) between s- and v-zones, we obtain an expression for the overall rate of the decomposition of BP:

$$-\frac{dc}{dt} = k_0 c + k_c c_m^2. \quad (13)$$

Eqn (13) can serve as a theoretical justification for the experimental data reported earlier.²² It confirms the kinetic non-equivalence of the catalytic effects of ionol and bisphenol 2246.

IV. Heterophase model for anaerobic chain decomposition of polypropylene hydroperoxide

The concept of heterophase chain reaction also proved to be fruitful in the analysis of ageing and stabilisation processes in polymers. Important characteristic features of autooxidation of polyalkenes and of decomposition of polymeric hydroperoxides under conditions of high and low fluctuation dynamics in a polymer-chain sponge have been rationalised in terms of this concept.⁴⁻⁶ Here, we consider the mechanism of chain decom-

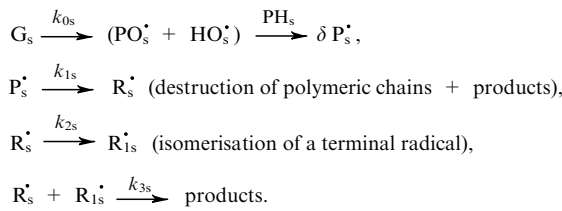
position of polypropylene hydroperoxide in the absence of oxygen dissolved in the polymer.

Polypropylene (PP) differs from glassy polymers in that its amorphous phase exists in a highly elastic state even at ambient temperature. The amorphous phase consists of separate areas surrounded by crystallites. The crystalline phase ($T_{\text{melt}} \approx 438 \text{ K}$) usually accounts for 60 mass % of isotactic PP. Separate crystallites are joined in a continuous rigid framework, which imparts properties of a solid to the polymer. In samples of PP with this structure, the processes of oxidation and decomposition of admixtures occur mostly in highly elastic areas.^{14, 15}

The rigid framework of crystallites influences in some way the structure of the non-crystalline phase of PP;²⁴ however, characteristic features of the chain-micellar sponge structure of the amorphous areas are retained. It cannot be ruled out that wide s-micropores in PP are also formed as layers near the surface of crystallites;²⁴ however, the greater part of the sponge micelles must consist of flexible chains as grains with more or less narrow v-micropores. Assuming that the chain-micellar sponge in polyalkenes retains its microheterogeneous structure, one should expect that the characteristic non-equivalence of the rates of radical generation in v- and s-zones will be manifested. In fact, it has been shown^{4-6, 25} that PP contains s-zones in which hydroperoxide dissociates much more rapidly than in v-zones. A primary reaction chain generated in v-zones induces chain reaction in v-zones due to the s,v-injection of radicals, the probability of which is relatively low. In rigid PP specimens, the heterophase chemical induction stops at the instant when the hydroperoxide accumulated in s-zones is entirely exhausted.

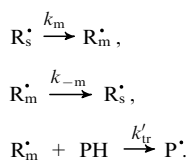
However, in the general case, decomposition of polypropylene hydroperoxide is not terminated at this point; its heterogeneous-heterophase stage, which has come to an end, is replaced by a slower heterogeneous-homophase stage. The occurrence of the latter stage is due to the fact that in v-zones a possibility exists that v-micropores will grow up to the size of s-micropores, due to fluctuations. At this stage, the frequency of the acts of hydroperoxide dissociation is largely determined by the conditions under which the polymeric specimens were prepared and by the residual mechanical tension in them.

An adequate s-scheme for the transformation of hydroperoxide (G) based on the results reported in a number of studies^{4-6, 25} has the following form:



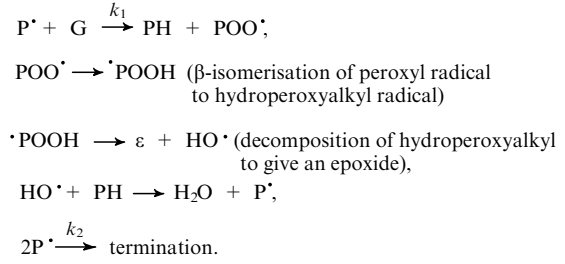
Here, the designation PH_s corresponds to the reactive CH groups at tertiary and secondary carbon atoms in the polymeric chains; δ is a coefficient of the yield of radicals upon dissociation of hydroperoxide; $P_s^\bullet$ are internal macroradicals; and $R_s^\bullet$ and $R_{1s}^\bullet$ are terminal macroradicals.

The probability for the transfer of a free valence from s-zones to v-zones is low, and, according to the tr-scheme, this transfer is largely accomplished by the most mobile and most reactive terminal radicals $R_s^\bullet$.



The $R_s^\bullet$ radicals, which exchange their positions within the s-framework and in the micropore bulk during vibrations ($R_m^\bullet$), are capable of reacting with CH bonds in v-zones.

Owing to this transfer of radicals, chain decomposition of hydroperoxide yielding water occurs in v-zones; this process can be described by the following v-scheme



By applying the condition of steady-state concentration of radicals to these block schemes, one can obtain a series of equations:

(a) for the concentration of the radicals translating the free valence

$$[R_s^\bullet] = \frac{\delta k_{0s} g_s}{2k_{2s}},$$

(g_s is the concentration of G in s-zones);

(b) for the rate of s,v-transfer

$$V_{tr} = k'_{tr}[PH][R_m^\bullet] = k_{tr}[R_m^\bullet] = k_{tr}k_m \frac{[R_s^\bullet]}{k_{-m} + k_{tr}} = \frac{k_{tr}k_m \delta k_{0s} g_s}{2k_{2s}(k_{-m} + k_{tr})}$$

(V_{tr} is equal to the rate of termination of the reaction v-chains, $V_{tr} = 2k_2[P^\bullet]^2$);

(c) for the concentration of radicals that attack hydroperoxide

$$[P^\bullet] = \left(\frac{V_{tr}}{2k_2} \right)^{0.5};$$

(d) for the rate of chain decomposition of hydroperoxide in v-zones

$$-\frac{dg_v}{dt} = k_1 [P^\bullet] g_v = k'_e g_s^{0.5} g_v.$$

Taking into account the facts that the current concentration of the hydroperoxide dissociating in s-zones is described by an exponential equation

$$g_s = g_{s0} \exp(-k_{0s} t),$$

and that the content of hydroperoxide in s-zones is low compared to that in v-zones, the latter being nearly equal to its concentration in the amorphous phase ($g_v \approx g$), we obtain the following expression for the rate of hydroperoxide decomposition:

$$-\frac{dg}{dt} = k'_e g_{s0}^{0.5} g \exp(-0.5 k_{0s} t) = k_e g \exp(-0.5 k_{0s} t). \quad (14)$$

Integration of Eqn (14) leads to an equation describing the curve of anaerobic decomposition of hydroperoxide:

$$g = g_0 \exp \left\{ \frac{k_e}{0.5 k_{0s}} [\exp(-0.5 k_{0s} t) - 1] \right\}. \quad (15)$$

At $t \rightarrow 0$, formula (15) is approximated by a first-order equation

$$g = g_0 \exp(-k_e t), \quad (16)$$

while at $t \rightarrow \infty$, it describes termination of the process in the presence of unconsumed hydroperoxide:

$$g_\infty = g_0 \exp \left(-\frac{k_e}{0.5 k_{0s}} \right).$$

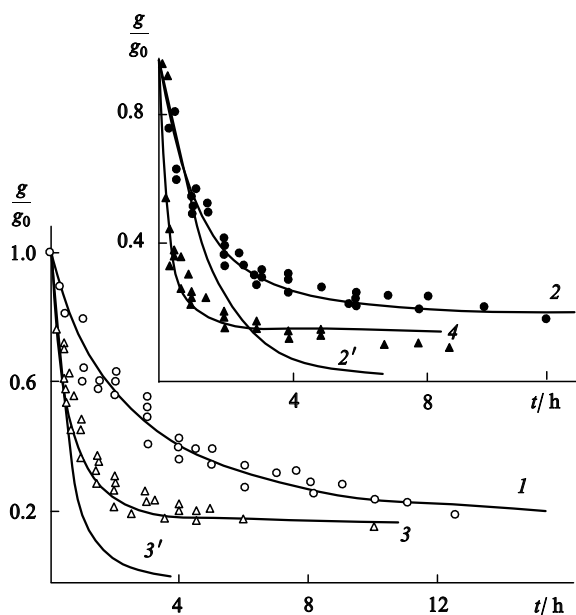


Figure 8. Curves for the consumption of polypropylene hydroperoxide in evacuated samples at temperatures /K: 383 (1); 393 (2, 2'); 403 (3, 3'); 413 (4). Curves 2' and 3' were calculated from a first-order equation for rate constants of 2.0×10^{-4} and $4.2 \times 10^{-4} \text{ s}^{-1}$, respectively.

Eqn (15) derived theoretically is in good agreement with experimental results, which is illustrated by the data presented in Fig. 8. The effective rate constants for chain decomposition at 383, 393, 403 and 413 K are equal to 0.865×10^{-4} , 2.00×10^{-4} , 4.20×10^{-4} and $10.00 \times 10^{-4} \text{ s}^{-1}$, respectively and are described by the general formula

$$k_e = 3.9 \times 10^9 \exp\left(-\frac{E_e}{RT}\right), \quad (17)$$

where $E_e = 100 \pm 5 \text{ kJ mol}^{-1}$. The rate constants for spontaneous decomposition at the same temperatures are 1.14×10^{-4} , 2.48×10^{-4} , 5.06×10^{-4} and $10.00 \times 10^{-4} \text{ s}^{-1}$, respectively, and are described by the following formula

$$k_{0s} = 6.5 \times 10^8 \exp\left(-\frac{E_{0s}}{RT}\right), \quad (18)$$

where $E_{0s} = 93.6 \pm 5 \text{ kJ mol}^{-1}$. For comparison, curves 2' and 3' calculated from formula (16) are presented in Fig. 8. It can be seen that these curves begin to deviate from the experimental points rather early; therefore, they lead to overestimated rates at large degrees of conversion, whereas theoretical curves 2 and 3, which are in agreement with experimental results, attest to almost complete termination of the process.

It should be noted that the first adequate description of the initial stage of anaerobic decomposition of hydroperoxide, which is characterised by Eqn (16), has been given only recently.⁶ This stage has long been regarded as a stage of spontaneous decomposition of hydroperoxide.¹⁴ Later, after its chain mechanism had been proved,^{15, 26} this stage has been believed to be a superposition of spontaneous and chain reactions having a one and one half order with respect to hydroperoxide. However, in both cases the initial stage of the anaerobic decomposition of hydroperoxide was considered within the framework of a homogeneous model. Since the results obtained earlier^{4–6, 25} indicate that this process occurs by a heterophase mechanism, we shall attempt to demonstrate that the regularities of the hydroperoxide decomposition accelerated by an admixture initiator are also quite consistent with the heterophase model.

The dependence of the initial rate of hydroperoxide decomposition on the concentration of dibenzoyl peroxide present as an admixture^{15, 26} evidences that the process includes a chain constituent characterised by quadratic termination of reaction chains:

$$V_0 = k_d g_0 + k_{ind} g_0 (k_b c_0)^{0.5}, \quad (19)$$

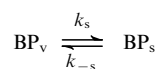
where g_0 and c_0 are initial concentrations of hydroperoxide and BP, respectively ($c_0 < 0.05 \text{ mol kg}^{-1}$), k_d is the rate constant for spontaneous decomposition of hydroperoxide, and k_b is the effective rate constant for the decomposition of BP.

Experimental values of k_d at 365 K obtained in the absence of BP and by extrapolating dependence (19) to $c_0 = 0$ are in agreement with each other and amount to $(1.8–1.9) \times 10^{-5} \text{ s}^{-1}$. With the assumption that a polymeric medium being oxidised can be regarded as a homogeneous liquid, the following expression was proposed^{15, 26} to describe the rate of the process occurring without BP:

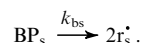
$$-\frac{dg}{dt} = k_d g + k'_e g^{1.5}, \quad (20)$$

The first term in this expression corresponds to spontaneous decomposition, while the second term reflects chain decomposition. At the same time, the rate constant for the chain reaction at 365 K calculated from formula (17) found by us, $k_e = 1.9 \times 10^{-5} \text{ s}^{-1}$, exactly coincides with the value of k_d in Eqn (19). In addition, Eqn (20) is at variance in its physical meaning with expression (15), which implies that the contribution of spontaneous decomposition of hydroperoxide is negligibly small compared to the contribution of the chain reaction.

Let us consider this situation in terms of a heterophase reaction mechanism. Recall that BP molecules rapidly migrate between the zones of chain sponge micelles,



and dissociate in s-zones,

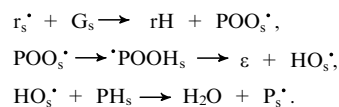


The condition for the equilibrium in the interzone exchange of BP molecules has the following form

$$c_s = \frac{k_s}{k_{-s}} c_v = K_e c_v = \frac{K_e c}{\beta}, \quad (21)$$

where c_s , c_v and c are concentrations of BP in s- and v-zones and in the amorphous phase of PP, respectively; β is the fraction of the amorphous phase in the polymer, and K_e is the equilibrium constant.

Owing to dissociation of BP, benzoyloxyl radicals with a free valence on the oxygen atom are generated in s-zones of the polymeric-chain sponge. The reactivity of these radicals with respect to the hydrogen atoms in OOH groups is known to be hundreds or thousands times higher than that towards CH groups.²⁷ Therefore, at the initial stage of the process, capture of benzoyloxyl radicals by hydroperoxides should be the predominant reaction in s-zones containing hydroperoxides.



Taking these transformations into account within the above s-scheme for decomposition of hydroperoxide, it is not difficult to derive an expression for the concentration of radicals that are leaders in the s,v-transfer of valence

$$[R_s^*] = \frac{\delta k_{0s} g_s + 2 k_{bs} c_s}{2 k_{2s}},$$

as well as for the rate of s,v-transfer

$$V_{tr} = \frac{k_{tr}k_m[R_s^*]}{k_{-m} + k_{tr}} = \frac{k_{tr}k_m(\delta k_{0s}g_s + 2k_{bs}c_s)}{(k_{-m} + k_{tr})2k_{2s}}.$$

Then using the v-scheme considered above and applying the condition of equality of the rates of v-chain generation and termination $V_{tr} = 2k_2[P^*]^2$, we find the concentration of the radicals that induce the decomposition of hydroperoxide

$$[P^*] = \left(\frac{V_{tr}}{2k_2}\right)^{0.5},$$

and the rate of chain reaction

$$-\frac{dg}{dt} = k_1[P^*]g = \frac{k_1g[k_{tr}k_m(\delta k_{0s}g_s + 2k_{bs}c_s)]^{0.5}}{[4k_2k_{2s}(k_{-m} + k_{tr})]^{0.5}}. \quad (22)$$

To pass from the specific rate of decomposition of BP

$$-\frac{dc_s}{dt} = 2k_{bs}c_s \quad (23)$$

to the empirical rate dc/dt , we express the number of moles of BP in s-zones as $p_s = m_s c_s$ (where m_s is the mass of s-zones) and take into account the fact that the loss of p moles of BP in a specimen is equal to the loss of the corresponding number of moles in s-zones (oxygen completely inhibits chain decomposition of BP in polypropylene).²⁸ Then

$$-\frac{dc}{dt} = -\frac{1}{m} \frac{dp}{dt} = -\frac{1}{m} \frac{dp_s}{dt} = -\frac{m_s}{m} \frac{dc_s}{dt}.$$

By substituting expressions (23) and (21) in this equation, we obtain

$$-\frac{dc}{dt} = \frac{2k_{bs}m_s K_e c}{\beta m} = k_b c. \quad (24)$$

The effective rate constant for decomposition of BP included in Eqn (24),

$$k_b = \frac{2k_{bs}m_s K_e}{\beta m}$$

in conformity with the known formula,

$$k_b = 8.4 \times 10^{13} \exp \frac{-124000}{RT} \text{ s}^{-1}$$

is equal to $1.2 \times 10^{-4} \text{ s}^{-1}$.

This value is consistent with the statement that the parameter

$$2k_{bs} = \frac{k_b m \beta}{m_s K_e}$$

is much greater than the k_b constant, because

$$\frac{m}{m_s} \gg 1 \text{ and } K_e < 1.$$

From this it follows that in Eqn (22), the rate of radical generation due to dissociation of BP is substantially higher than that due to dissociation of hydroperoxide. According to formula (18), the rate constant for spontaneous decomposition of hydroperoxide at 365 K, k_{0s} , is equal to $2.6 \times 10^{-5} \text{ s}^{-1}$. In other words, for a fairly wide range of initial concentrations of BP, Eqn (22) is transformed into the following equation

$$-\left(\frac{dg}{dt}\right)_0 = k_{ind} g_0 (k_b c_0)^{0.5};$$

and only in the region of very low c_0 , is it extrapolated to relation (14), which also characterises chain decomposition of hydroperoxide with quadratic termination of reaction v-chains.

Thus, the heterophase scheme for hydroperoxide decomposition stimulated by dibenzoyl peroxide provides an explanation of the kinetic results obtained in previous studies^{15,26} and discloses the intimate connection between the mechanism of this process and the mechanism of non-sensitised chain reaction. In addition, this scheme makes it possible to account for the formation of water in the chain process, which has not been reflected in the homogeneous scheme at all.

V. The mechanism of the influence of ionol on the rate of anaerobic decomposition of polypropylene hydroperoxide

In an early paper,²⁹ some interesting features of the fast and slow kinetic stages in the unified process of decomposition of polypropylene hydroperoxide in the presence of ionol have been found. The researchers used low-molecular-weight syndiotactic PP ($M_n = 13\,500$), which was oxidised at 373 K, in order to accumulate hydroperoxide, by passing oxygen through its solution in chlorobenzene containing an initiator.

In the absence of oxygen, decomposition of the hydroperoxide thus accumulated occurred in two stages, the first of which was fast, while the second stage was slow. The rate of the second stage of hydroperoxide decomposition, unlike that found for PP samples oxidised in the bulk (Fig. 8), was quite measurable.

The rate of the fast stage did not depend on the concentrations of hydroperoxide and ionol. In fact, at $T = 408 \text{ K}$ and at the following concentrations of reagents, G/IH (mol litre^{-1}) 0.0078/0.001, 0.0034/0.001, 0.27/0.1 and 0.005/0.012, the rate constants k_{e1} for this stage were 19.8×10^{-4} , 15.1×10^{-4} , 19.8×10^{-4} and $18.2 \times 10^{-4} \text{ s}^{-1}$, respectively; at $T = 393 \text{ K}$ and at concentrations G/IH (mol litre^{-1}) of 0.034/0.000, 0.011/0.001, 0.0078/0.001 and 0.27/0.01, the rate constants k_{e1} were 5.01×10^{-4} , 6.3×10^{-4} , 6.41×10^{-4} and $6.13 \times 10^{-4} \text{ s}^{-1}$, respectively.

Conversely, the rate constant for the second stage k_{e2} (which is formally a first-order rate constant) depended on the initial concentration of hydroperoxide g_0 , as has also been observed in the homogeneous chain reaction; however, unlike the latter case, the constant k_{e2} did not change when ionol was present in small or medium concentrations (up to $0.05 \text{ mol litre}^{-1}$). Only at a very high content of ionol ($0.124 \text{ mol litre}^{-1}$), the rate of the second stage lost its chain constituent, and the constant k_{e2} assumed its minimum value equal to that observed in the absence of ionol and at the lowest concentration g_0 .

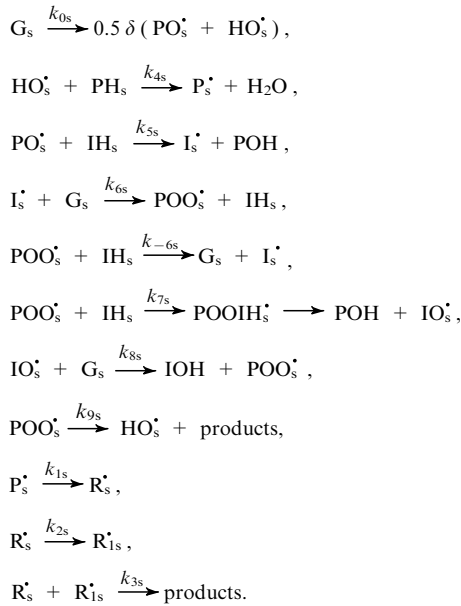
It was suggested²⁹ that at the first stage, hydroperoxide decomposition follows a chain mechanism, which is characterised by a specific mode of propagation of reaction chains along the polymer. However, it was not explained why the fraction of the rapidly decomposing hydroperoxide diminished from 0.8–0.9 to 0.25 upon the introduction of ionol in a concentration of up to $0.124 \text{ mol litre}^{-1}$.

From our viewpoint, the reaction studied in Ref. 29 actually follows a chain mechanism, its specific features reflecting the specific state of the reaction matrix, namely, the chain-sponge micellar structure of the oxidised PP. It should be noted that the local concentration of hydroperoxide in s-zones, g_{s0} , which appears in Eqn (14), reaches the level of saturation during the oxidation of PP. As has been found in a previous study,⁶ this is accompanied by the constant k_e reaching its maximum value, equal to $11.0 \times 10^{-4} \text{ s}^{-1}$, at 403 K. Eqn (17) makes it possible to calculate the constants k_e at 408 and 393 K (the effective activation energy E_a is 100 kJ mol^{-1}). The values of 16×10^{-4} and $5.15 \times 10^{-4} \text{ s}^{-1}$ thus obtained coincide with those found for k_{e1} in Ref. 29. This indicates that the limiting degree of filling of s-zones with hydroperoxide was achieved in the oxidation in

solution carried out in this study. This is why the rate constant for the initial stage of chain decomposition k_e was independent of the initial concentration g_0 calculated with respect to the whole specimen [Eqns (14) and (16)].

Regarding the specific character of the fast stage of the process in the presence of ionol, we recall that ionol substantially narrows the concentration range in which the fast stage occurs, but does not change the magnitude of k_{e1} . Within the framework of the heterophase model, this can be accounted for by the fact that ionol, which has no influence on the mechanism of the transfer of radicals from s-zones to v-zones, decreases the number of radicals transferred due to the appearance of the additional catalytic pathway for destruction of the hydroperoxide accumulated in s-zones.

All the foregoing can be expressed as an s_i -scheme by introducing the reactions involving ionol into the s-scheme described above:

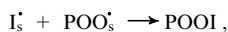


This scheme reflects a number of characteristic features of the reactants. The reactions of ionol with alkyl radicals $P_s^\bullet$, $R_s^\bullet$ and $R_{1s}^\bullet$ were not included in the scheme, because all alkylphenols exhibit fairly low reactivities towards radicals derived from polyalkenes¹⁴ (even bisphenol 2246, which is more reactive, does not have any influence on the concentration of PP radicals, which eliminate propene during the induction period of the PP oxidation).³⁰

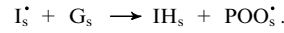
The scheme takes into account the interaction of phenoxyl with hydroperoxide^{15,16} and both routes known from the literature for the attack of a phenol molecule by $POO^\bullet$ radicals: to yield phenoxyl and σ -complex. In the micropores of chain-sponge micelles, unlike liquid solutions, there exist molecular force fields, which, as noted above, hamper reversible dissociation of σ -complexes and thus enable their subsequent transformations. In the present case, σ -complex is converted into the alkoxyl radical $IO^\bullet$ with a quinoid structure.

This scheme also takes into account the fact that $HO_s^\bullet$ radicals are highly reactive and interact with the polymer more quickly. Since they are adsorbed on the walls of s-micropores, the conditions for their reaction with ionol are less favourable than those of $PO_s^\bullet$ radicals.

Finally, due to the high local concentration of hydroperoxide in the s-zones of the samples used in Ref. 29, the s-scheme did not include recombination



the rate of which at the initial stage of the process is believed to be negligibly small compared to the rate of the reaction



If the condition of a steady-state concentration of radicals is applied to the s_i -scheme, it can be easily seen that the expression for the concentration of radicals

$$[R_s] = \frac{\delta k_{0s} g_s}{2 k_{2s}},$$

which has been obtained previously based on the s-scheme for the process occurring without ionol (see Section IV), also holds in the present case. The concentration of s-phenoxyl radicals corresponding to the s_i -scheme does not depend on the concentration of G_s

$$[I_s] = \frac{0.5 \delta k_{0s}}{k_{6s}} + \frac{0.5 \delta k_{0s} k_{-6s} [IH_s]}{k_{6s} k_{9s}}, \quad (25)$$

the concentration of s-peroxyl radicals is equal to

$$[POO_s^\bullet] = \frac{0.5 \delta k_{0s} g_s}{k_{9s}},$$

and the overall rate for decomposition of s-hydroperoxide is the sum of several terms,

$$\begin{aligned}
 -\frac{dg_s}{dt} &= k_{0s} g_s + k_{6s} [I_s] g_s + k_{8s} [IO_s^\bullet] g_s - k_{-6s} [POO_s^\bullet] [IH_s] = \\
 &= k_{0s} g_s + 0.5 \delta k_{0s} g_s + \frac{0.5 \delta k_{0s} g_s k_{7s}}{k_{9s}} [IH_s],
 \end{aligned}$$

the second term being much smaller than the first term characterising the spontaneous decomposition of G_s ($\delta < 1$). By integrating this expression and taking into account the condition of interzone equilibrium

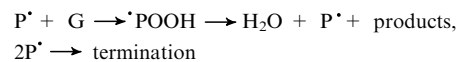
$$c_{is} = \frac{K_{ei} c_i}{\beta}$$

(where c_{is} ($[IH_s]$) and c_i ($[IH]$) are the concentrations of ionol in s-zones and in the non-crystalline phase of PP, respectively, K_{ei} is the equilibrium constant, and β is the fraction of the amorphous phase in the polymer), we obtain the equation for the consumption of s-hydroperoxide with allowance for the chain contribution catalysed by ionol:

$$g_s = g_{s0} \exp [-(k_{0s} + b_i c_i) t], \quad (26)$$

where b_i is a complex constant.

When we pass to the mechanism of chain decomposition of hydroperoxide in v-zones, it is noteworthy that, according to the study discussed above,²⁹ ionol exerts no influence on the constant k_{e1} over the whole range of concentrations c_i studied and has an influence on the constant k_{e2} only at a fairly high c_i value, 0.124 mol kg⁻¹. Therefore, it was suggested²⁹ that the reaction chains of hydroperoxide decomposition are mostly realised through the migration of the free valence along the polymer chains and that the intermolecular attack of hydroperoxide by $P^\bullet$ radicals yielding free peroxyl radicals is impossible. In this case, the v-scheme considered above assumes the following form



(the $OH^\bullet$ radical arising reacts with the neighbouring CH group of the same macromolecule). This scheme corresponds to a fairly loose packing of polymer chains in the chain-sponge micellar structure.

The structural looseness, *i.e.* an enhanced volume tension of the chain sponge in the PP specimens oxidised in solution, is stabilised due to fixing of the stretched chains on the crystallite

framework. It is known that syndiotactic and isotactic PP readily crystallise; and crystallising polyalkenes do not form molecular solutions in hydrocarbons at $T < T_{\text{melt}}$.³¹ They are able to be dispersed in a liquid to some extent to form a colloidal solution, in case where polymer–polymer type molecular contacts arise in the system leading to the simultaneous formation of crystal nuclei.³²

Thus, in all probability, the PP matrix subjected to oxidation in the study considered above²⁹ consisted of disseminations of chain-sponge micelles swelled in chlorobenzene into colloidal particles reinforced by a lattice of crystallites linked to one another. The lattice of crystallites was relatively strong and did not change upon drying and heating of the suspension.

It is the framework strength of the lattice of crystallites that accounts for the stabilisation of the structural looseness of chain-sponge micelles and for the fact that the rates of decomposition of hydroperoxide in PP occurring as a colloidal suspension in chlorobenzene and in PP films are virtually identical.²⁹

The reaction v-scheme for hydroperoxide decomposition, modified with allowance for the results discussed above,²⁹ includes the same steps of generation and termination of reaction v-chains, which were considered in Section IV. Therefore, Eqn (26) presented above can be included in the expression for the rate of the chain reaction, which was proposed in Section IV:

$$-\frac{dg}{dt} = k_1[P^\cdot]g = k'_e g_s^{0.5} g = k_e g \exp[-0.5(k_{0s} + b_1 c_1)t]. \quad (27)$$

The pre-exponential factor k_e in Eqn (27) has the same structure as that in Eqn (14), and the exponential part contains an additional constant, $b_1 c_1$, associated with chain decomposition of hydroperoxide in s-zones.

Integration of Eqn (27) leads to a formula, which describes the curve for decomposition of hydroperoxide

$$\ln \frac{g}{g_0} = \frac{k_e}{0.5(k_{0s} + b_1 c_1)} \{ \exp[-0.5(k_{0s} + b_1 c_1)t] - 1 \}.$$

At $t \rightarrow 0$, i.e. in the initial stage of the reaction, this formula is transformed in a first-order equation

$$\ln \frac{g}{g_0} = -k_e t,$$

or

$$g = g_0 \exp(-k_e t),$$

which coincides with Eqn (16) and includes only the constant k_e , which does not depend on the content of ionol.

At a high degree of conversion ($t \rightarrow \infty$), this initial formula is transformed in the following expression

$$\ln \frac{g_\infty}{g_0} = -\frac{k_e}{0.5(k_{0s} + b_1 c_1)},$$

or

$$g_\infty = g_0 \exp \left[-\frac{k_e}{0.5(k_{0s} + b_1 c_1)} \right],$$

which characterises a 'kinetic step'; the larger the ionol concentration (c_1) in the samples and the more pronounced is the catalytic influence of ionol on the decomposition of hydroperoxide in s-zones, the higher is this step.

Now we shall consider characteristic features of the homophase stage of decomposition of PP hydroperoxide.

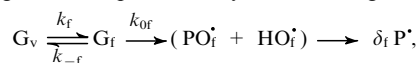
In the study discussed above,²⁹ the fast stage of the process was followed by its slow stage rather than by its kinetic termination. The rate of the slow stage remained constant at low and medium concentrations of ionol (up to 0.05 mol kg⁻¹). The fact that the rate of the reaction characterised by k_{e2} can be reliably measured, although it is relatively low, distinguishes these samples from the samples oxidised in the bulk in which the second stage of the process occurs at an extremely low rate (see Fig. 8).

In the first stage of the process, the rate of hydroperoxide decomposition in the samples, which were studied in Ref. 29, was also higher than that in PP oxidised in the bulk (the temperature being the same). Obviously, the higher reactivity of the polymer oxidised in suspension should be attributed to the loose packing of the polymer chains in the chain-sponge micellar structure.

The loose structure of the micellar material in combination with high flexibility of the polymer chains increases the degree to which v-zones (which accumulate the greater part of the hydroperoxide formed upon oxidation) are ready to undergo thermofluctuational excitation, which ensures widening of v-micropores to the size of s-micropores. Consequently, the frequency of these excitation acts increases and the probability of dissociation of hydroperoxide groups within the intensely oscillating micropores increases correspondingly.

Thermofluctuational excitation of this sort is favourable for the beginning of the second stage of hydroperoxide decomposition, which can be characterised as a heterogeneous-homophase stage. The contribution of this stage becomes predominant after heterophase s,v-transfer of radicals has ceased due to the exhaustion of hydroperoxide groups within s-zones.

There is always a certain probability of the flickering growth of v-micropores in the chain-sponge zones; this probability is especially high when the polymer occurs in the highly elastic or molten state.^{5,6} The process of generation of free radicals in this stage can be represented by the following scheme



in which the constants k_f , k_{-f} and k_{of} correspond to the heterogeneous steps of excitation, deactivation and dissociation of hydroperoxide groups conjugated with the steps of fluctuation of micropores; the symbol δ_f denotes the fraction of radicals leaving an oscillating micropore.

An equation for the rate of chain heterogeneous-homophase reaction follows from this scheme in combination with the reaction v-scheme considered in Section IV:

$$-\left(\frac{dg}{dt}\right)_c = k_1[P^\cdot]g = k_1 g^{1.5} \left[\frac{\delta k_{of} k_f}{2 k_2 (k_{-f} + k_{of})} \right]^{0.5}.$$

Taking into account the fact that the occurrence of this reaction suggests a relatively large contribution of fluctuational dissociative decomposition of hydroperoxide in v-zones, we obtain the following expression for the overall rate of decomposition:

$$-\frac{dg}{dt} = k_{d,f} g + k_{c,f} g^{1.5}, \quad (28)$$

where $k_{d,f}$ and $k_{c,f}$ are complex rate constants for non-chain and chain v-reactions, respectively.

The fact that the process actually obeys Eqn (28) is indicated by the typical dependence of the formal first-order rate constant on the initial concentration of hydroperoxide, which was found in Ref. 29:

$$k_{e2} = k_{d,f} + k_{c,f} g_0^{0.5}.$$

Note that Eqn (28) looks like Eqn (20) obtained for a homogeneous reaction; however, in contrast to the interpretation reported previously,^{15,26} it characterises the slow stage of decomposition of a polymeric hydroperoxide rather than its fast stage.

According to the data obtained in Ref. 29, the chain constituent of the rate $k_{c,f} g_0^{0.5}$ is suppressed by ionol only when its concentration is very high, $c_1 = 0.124$ mol kg⁻¹. This can be explained by the fact that ionol is extremely inert with respect to alkyl polymeric radicals $P^\cdot$ and that the probability of its interaction with $PO_i^\cdot$ and $HO_i^\cdot$ radicals, hanging on the walls of a micropore excited by thermofluctuation, is low.

VI. Specific features of the influence of ionol on the chain decomposition of polypropylene hydroperoxide in the presence of oxygen

The presence of dissolved oxygen in the oxidised PP samples containing ionol dramatically changes the situation; in this case, the heterogeneous-homophase process is brought to the fore. As shown in the previous section, this process is limited by the slow rate of heterogeneous generation of radicals, occurring directly in those structural zones of chain-sponge micelles, which accumulate the major part of hydroperoxide resulting from the oxidation of PP. The chain decomposition of hydroperoxide initiated in the absence of oxygen is decelerated by ionol only when its concentration is very high, because the reactivity of alkyl radicals towards ionol is negligibly small.

The situation changes in the presence of oxygen, which converts alkyl radicals into peroxy radicals and thus sharply increases the rate of their interaction with ionol and simultaneously switches the process to the catalytic decomposition of hydroperoxide.

An example of this change in the kinetic regime of a reaction has been reported by Chien and Boss,²¹ who studied the kinetics of hydroperoxide decomposition in films, which were prepared from a melt and then oxidised (G_1) or obtained from colloidal PP oxidised in chlorobenzene (G_2). The introduction of ionol into these specimens caused the appearance of induction periods in their oxidation carried out by heating under an atmosphere of oxygen ($P_{O_2} = 1$ atm), the duration of these periods being substantially different for the specimens prepared in different ways. The rates of hydroperoxide decomposition during the induction periods were also different. The films of the polymer oxidised in a colloidal solution were the most active. This is not surprising, since chain-sponge micelles in these films possess the most pronounced fluctuation-dynamic properties (see Section V).

Figure 9 shows the plot for the consumption of G_1 (curve 1) in samples with weak fluctuation dynamics ($T = 403$ K, $g_0 = 0.150$ mol litre⁻¹, $c_{i0} = 0.013$ mol litre⁻¹). It can be compared with the curve for the consumption of peroxy radicals (curve 2) and with the curves recorded after completion of the

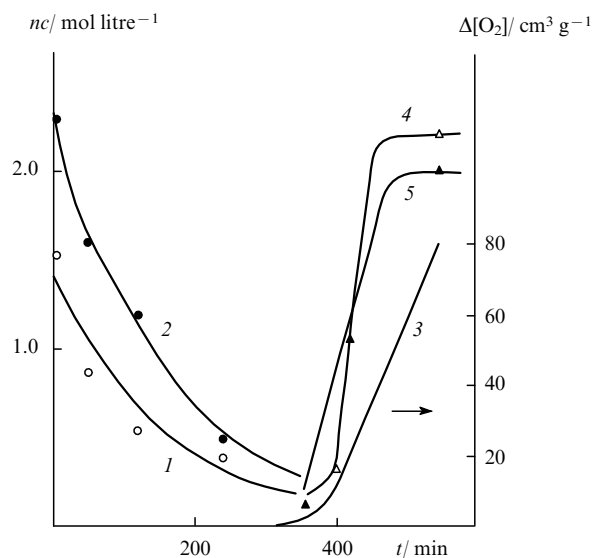


Figure 9. Kinetic curves for autooxidation of PP during the induction period (1, 2) and after it (3–5) at 403 K ($P_{O_2} = 1$ atm): consumption of hydroperoxide (1); consumption of phenoxyl radicals derived from ionol (2); consumption of oxygen (3); accumulation of hydroperoxide (4); accumulation of peroxy radicals (5). The factor n for curves 1, 4 is 10; that for 2, 5 is 10^6 .

induction period for the absorption of oxygen (3) and for the accumulation of hydroperoxides and polymeric peroxy radicals (4 and 5, respectively).

During the induction period, which lasted for 350 min, the amount of oxygen absorbed did not exceed the sensitivity threshold of the analytical instrument used. In this stage, the kinetic curve for the consumption of ionol (which is not shown in Fig. 9) and the curve for the consumption of phenoxyl radicals are described by exponential equations $c_i = c_{i0} \exp(-k_i t)$ and $[I] = [I]_0 \exp(-k_i t)$, respectively, with identical coefficients $k_i = 1 \times 10^{-4} \text{ s}^{-1}$. This combination of kinetic curves implies that the condition of a quasi-steady-state concentration of phenoxyl radicals derived from ionol is ensured almost from the very beginning of the process and that phenoxyl radicals do not participate in the steps of bimolecular destruction and do not react with oxygen.

During the induction period, the concentration of $POO\cdot$ radicals was lower than the limit of sensitivity of the EPR spectrometer ($\leq 10^{-8} \text{ mol litre}^{-1}$), but when the induction period was over, it quickly reached a steady-state value of $\sim 2 \times 10^{-6} \text{ mol litre}^{-1}$, which could be measured reliably.

No analytical function has been suggested²¹ to describe the curve of consumption of G_1 ; however, with allowance for the usual 10% error in the determination of hydroperoxide concentration, a calculated curve can be constructed (curve 1 in Fig. 9), which follows an exponential law with the same k_i value that characterises consumption of ionol and phenoxyl radicals:

$$g = g_0 \exp(-k_i t) \quad (29)$$

(the value $g_0 = 0.14 \text{ mol litre}^{-1}$ was taken as the initial concentration). A transformed version of this equation plotted on semi-logarithmic coordinates is shown in Fig. 10 (straight line 1), together with the plots obtained by us, which describe the consumption of hydroperoxide in the presence of air and tri-*tert*-butylphenol. Our experiments were aimed at obtaining a more precise pattern for the scattering of experimental points, because the number of points obtained in the study cited²¹ was insufficient.

In our experiments, weighed portions of finely grained PP powder (~ 1 mg each) were oxidised in air at 413 K until the concentration of hydroperoxide was $g_0 = 0.14 \text{ mol kg}^{-1}$. Tri-*tert*-butylphenol was introduced in the oxidised powder as a solution in chloroform. After 40 min of storage, the solvent was evaporated and its last traces were removed *in vacuo*. Decomposition of the hydroperoxide was studied by heating the samples in air and using the spectrophotometric version of iodometric analysis.^{4–6, 25} The curves obtained for the consumption of hydroperoxide at phenol to polypropylene ratios of 1 : 1 and 2 : 1 by weight were identical.

The experimental points on the straight lines 2, 3, 4 and 5 (Fig. 10) were obtained at 372, 383, 393 and 403 K, respectively. For comparison, the initial section of the transform of the curve

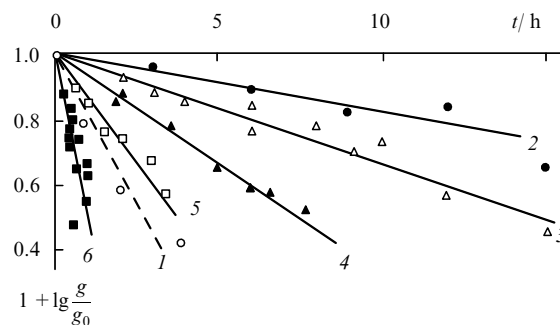


Figure 10. Constants from the curves for the consumption of hydroperoxide in the presence (1–5) and in the absence (6) of oxygen in PP samples containing ionol (1), tri-*tert*-butylphenol (2–5) and containing no antioxidant (6) at temperatures/K: 372 (2); 383 (3); 393 (4); 403 (1, 5, 6).

for decomposition of hydroperoxide at 403 K in the absence of oxygen is also presented (straight line 6). Comparison of the scatter of experimental points in our experiments with that observed in the previous study²¹ (straight line 1) makes it possible to conclude that the use of exponential functions (29) is acceptable in all cases. The effective rate constants k_i calculated from the slopes of the straight lines 2–5 are the following: 0.85×10^{-5} , 2.0×10^{-5} , 4.26×10^{-5} and $8.5 \times 10^{-5} \text{ s}^{-1}$. They can be described by the following common expression

$$k_i = 6.0 \times 10^7 \exp\left(-\frac{E_i}{RT}\right),$$

where $E_i = 91.5 \text{ kJ mol}^{-1}$. It is significant that at 403 K, the rate constant for the decomposition of hydroperoxide in the presence of ionol k_i is equal to $1 \times 10^{-4} \text{ s}^{-1}$, which differs only slightly from the value of $0.85 \times 10^{-5} \text{ s}^{-1}$ found for the process involving tri-*tert*-butylphenol. Both of these constants are markedly smaller than the constant characterising the chain decomposition of hydroperoxide in the absence of oxygen and alkylphenol (Fig. 10, straight line 6), which is equal to $4.2 \times 10^{-4} \text{ s}^{-1}$. However, the decrease in the decomposition rate cannot be attributed to the partial reduction of hydroperoxide caused by chain oxidation of PP or by the interaction of peroxy radicals with an inhibitor, since the current concentrations g , c_i and $[I]$ are directly proportional to one another over the whole induction period. It is also significant that in this stage of the process, the chain consumption of oxygen is largely depressed (Fig. 9, curve 3), and the synchronous consumption of hydroperoxide and ionol characterised by identical exponential factor $\exp(-k_i t)$ takes place when the concentration g_0 is ten times higher than c_{i0} , *i.e.* under conditions when the formation of hydroperoxide in the steps of chain termination can by no means override the four-fold deceleration of its decomposition (Fig. 10, straight lines 1 and 6).

The kinetic law for the consumption of hydroperoxide, proposed by Chien and Boss,²¹ corresponds formally to a non-chain homogeneous reaction. However, the effective rate constant for this process falls in the range of rate constants for the heterophase stage of chain anaerobic decomposition⁶ and is many times higher than the rate constant for the heterogeneous-homophase stage of the non-chain constituent. The latter reaches only a value of $4 \times 10^{-5} \text{ s}^{-1}$ at 408 K or $1.5 \times 10^{-5} \text{ s}^{-1}$ at 393 K even for fluctuatonally active samples containing hydroperoxide G_2 ,²⁹ and in films with G_1 it cannot be reliably measured at all (Sections IV and V).

The dramatic increase in the rate of hydroperoxide decomposition in the presence of oxygen with respect to the rate of the second (homophase) stage of the anaerobic reaction is, most probably, due to oxidation of alkyl macroradicals to peroxy radicals. This process has no influence on the generation of radicals by the mechanism of thermofluctuational excitation of v-micropores but it sharply accelerates the interaction of polymer radicals with alkylphenols and results in the appearance of a new chain pathway to the decomposition of hydroperoxide. Recall that we had to introduce a new reaction in order to explain the characteristic features of the anaerobic decomposition of hydroperoxide in the presence of ionol, and this reaction was actually included in the s_i -scheme described in Section V. According to the s_i -scheme, the new chain reaction of hydroperoxide decomposition is induced by alkoxyl radicals with a quinoid structure of the six-membered carbon ring, which are formed from ionol.

The characteristic features of the decomposition of PP hydroperoxide under oxidative conditions, considered in this Section, also indicate that this new chain reaction should be taken into account. This conclusion is also confirmed by the fact, established independently, that in the specimens with G_2 , the process is accelerated by oxygen to even a greater degree. For example, it was found²⁹ that complete consumption of G_2 and of ionol-derived phenoxyl radicals under an oxygen atmosphere at $T = 393 \text{ K}$ ($g_0 = 0.156 \text{ mol litre}^{-1}$, $c_{i0} = 0.17 \text{ mol litre}^{-1}$) is

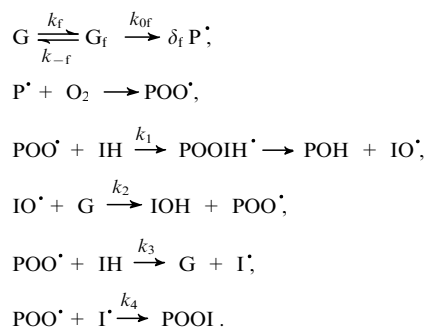
observed in approximately 20 min, whereas in samples with G_1 this occurs after 350 min, *i.e.* the half-transformation period decreases from 116 min to 5–10 min, despite the fact that G_2 decomposes at a lower temperature. The effective rate constant for the reaction under these conditions ($\sim 23 \times 10^{-4} \text{ s}^{-1}$) is markedly larger than the rate constant for the initial stage of chain anaerobic reaction in identical samples (see Section V).

Thus, the influence of oxygen leads phenomenally to the replacement of two macroscopic kinetic stages of the anaerobic process by a single stage; this is due to a substantial acceleration, which is dissimilar for G_1 and G_2 , of the ionol-catalysed decomposition of hydroperoxide in a process occurring by a chain mechanism.

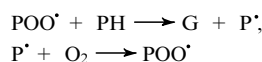
The generation of the reaction v-chains under oxidative conditions occurs predominantly according to a homophase route: *via* thermofluctuational excitation of v-micropores, which accumulate hydroperoxide. Ionol, which intercepts all the reaction chains and behaves as an efficient inhibitor of autooxidation of PP, participates simultaneously in the reaction chains of hydroperoxide decomposition.

It should be emphasised that the regularities of the decomposition of PP hydroperoxide both in the presence and in the absence of oxygen considered above rule out the possibility of any significant contribution of the molecular reaction of alkylphenol with hydroperoxide (and thus preclude an increase in the probability of degenerate branching in the presence of an inhibitor). In addition, the fact that the catalytic function of ionol is retained during the whole induction period indicates that some mechanism for its regeneration exists.

Taking the above into account, the following v_i -scheme can be proposed for the transformations that occur in v-zones of chain-sponge micelles of PP beginning with thermofluctuational excitation of v-micropores.



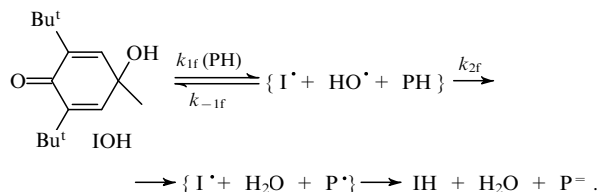
According to this scheme, the reaction chains of hydroperoxide decomposition propagate in the same way as those in the s_i -scheme considered above, *i.e.* through intermediate formation of a σ -complex from phenol and a peroxy radical and of a quinoid alkoxyl (the rate constants for these stages are k_1 and k_2 , respectively). However, chain termination in the v_i -scheme, unlike that in the s_i -scheme, occurs on ionol and its rate (characterised by constant k_3) is directly proportional to the rate of chain propagation in the decomposition of hydroperoxide. The latter is determined by the processes characterised by rate constant k_1 . It is this direct proportionality that accounts for the fact that ionol, which sharply decreases the concentration of peroxy radicals and brings the rate of chain autooxidation of PP



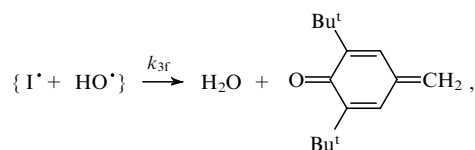
to a negligibly small value, ensures the catalytic development of chain decomposition of PP hydroperoxide.

Regeneration of the initial ionol (and tri-*tert*-butylphenol) from the product of its transformation, a quinoid alcohol, should follow a pathway ensuring regeneration of ionol from the quinoid compound Ir (see Sections II and III) in the steps of thermofluctuational excitation of v-micropores. These steps occur as

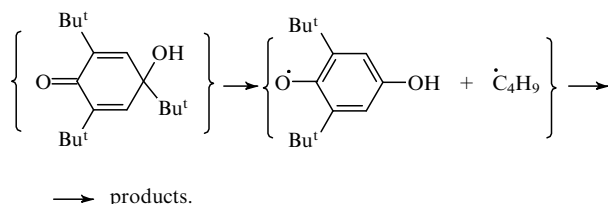
'latent radical' or 'intra-cage' processes and include dissociation of the quinoid alcohol and subsequent dehydrogenation of macro-molecules:



where $\text{P}^\bullet$ is a fragment of the polymer containing a double bond. Simultaneously, partial loss of phenol should occur in the disproportionation steps occurring in parallel. In the case of ionol, this leads to a methylenequinone



which undergoes subsequent transformations, while in the case of tri-*tert*-butylphenol, this process involves elimination of *tert*-butyl radicals to give a quinone and other products



By applying the condition of steady-state concentration to the reactive species appearing in the v_i -scheme (radicals and alcohols IOH), one can derive an expression for the equality of the chain generation and chain termination rates

$$\delta_f \alpha_f k_{of} g = 2 k_3 [\text{POO}^\bullet][\text{IH}]$$

[here δ_f is the yield of radicals in the fluctuation decomposition of hydroperoxide in v -zones, and $\alpha_f = k_f / (k_{-f} + k_{of})$] and for the rate of hydroperoxide decomposition

$$\begin{aligned}
 -\frac{dg}{dt} &= \alpha_f k_{of} g + k_1 [\text{POO}^\bullet][\text{IH}] - 2 k_3 [\text{POO}^\bullet][\text{IH}] = \\
 &= \alpha_f k_{of} g + \frac{k_1 \delta_f \alpha_f k_{of} g}{2 k_3} - \delta_f \alpha_f k_{of} g = k_{ii} g
 \end{aligned}$$

The latter expression implies that this process obeys first-order kinetics with respect to hydroperoxide and zero-order kinetics with respect to alkylphenol

$$g = g_0 \exp(-k_i t)$$

The rate of the consumption of phenol, according to the v_i -scheme, is

$$\begin{aligned}
 -\frac{dc_i}{dt} &= k_1 [\text{POO}^\bullet][\text{IH}] + k_3 [\text{POO}^\bullet][\text{IH}] - k_{2f} [\{ \text{I}^\bullet + \text{HO}^\bullet + \text{PH} \}] = \\
 &= \left[k_3 + \frac{k_1 k_{3f}}{k_{2f} + k_{3f}} \right] [\text{POO}^\bullet][\text{IH}] = \\
 &= \left[0.5 + \frac{0.5 k_1 k_{3f}}{(k_{2f} + k_{3f}) k_3} \right] \delta_f \alpha_f k_{of} g = k_{ii} g
 \end{aligned}$$

By integrating the expression

$$-\frac{dc_i}{dt} = k_{ii} g$$

we obtain the equation

$$c_i = \frac{k_{ii} g_0}{k_i} \exp(-k_i t) + \text{const};$$

for the initial instant $c_i = c_{i0}$ ($t = 0$), this equation assumes the following form

$$c_i = c_{i0} - \frac{k_{ii} g_0}{k_i} [1 - \exp(-k_i t)]$$

If at $t \rightarrow \infty$, $c_i = 0$, then

$$c_{i0} = \frac{k_{ii} g_0}{k_i} \quad \text{and} \quad c_i = c_{i0} \exp(-k_i t),$$

which is in full agreement with the results obtained by Chien and Boss.²¹

As noted above, a quasi-equilibrium concentration of phenoxyl radicals in the process under consideration is established very quickly. The kinetics of their consumption is described by the theoretical formula

$$[\text{I}^\bullet] = \frac{k_3 c_i}{k_4} = \frac{k_3 c_{i0}}{k_4} \exp(-k_i t),$$

which should be valid from the instant at which a quasi-steady-state concentration of phenoxyl radicals is established until the induction period in the PP oxidation is completed. This theoretical expression, like the previous ones, describes adequately the experimental results obtained in Ref. 21. Therefore, it can be concluded that the heterogeneous-homophase chain reaction model properly reflects the empirical regularities of the oxidative decomposition of polypropylene hydroperoxide in the presence of a phenolic antioxidant.

It is noteworthy that the mechanism of partial regeneration of phenol from the quinoid alcohol formed upon its chain transformation, which is similar to the mechanism of regeneration of ionol from the product of the reaction of phenol with dibenzoyl peroxide (Section II), is apparently fairly abundant. This has been supported by an independent experiment that we have carried out with the methyl ether of the quinoid alcohol, prepared from ionol by a procedure described previously.³³

When this ether was introduced into cellulose triacetate films together with dibenzoyl peroxide, it exerted qualitatively the same influence on the rate of BP decomposition as did alkylphenols (see Sections II and III). Fig. 11 shows the linear transforms of the curves for anaerobic decomposition of BP ($c_0 = 0.66 \text{ mol kg}^{-1}$, $T = 371 \text{ K}$) at initial concentrations of the methoxy-quinoid compound of 0.08 mol kg^{-1} (straight line 1) and 0.32 mol kg^{-1} (straight line 2). Even when the difference between the initial concentrations is so large, the effective rate constant for this reaction, as has also been observed for mixtures with phenols, remains virtually unchanged during the whole process. As in systems containing phenols, the rate of the chain reaction of BP induced by polymer radicals reaches a minimum when the concentration of the quinoid ether is $\sim 0.08 \text{ mol kg}^{-1}$. At quinoid ether concentrations of 0, 0.08 and 0.32 mol kg^{-1} , the effective rate constants for the decomposition of BP were 2.7×10^{-4} , 1.5×10^{-4} and $1.58 \times 10^{-4} \text{ s}^{-1}$, whereas the rate constant for non-chain decomposition of BP was $7.5 \times 10^{-5} \text{ s}^{-1}$. Thus, the non-phenolic quinoid compound exerts a prolonged inhibitory influence on the decomposition of BP induced by macroradicals and, conversely, exhibits a catalytic effect in the concentration range in which the influence of macroradicals is suppressed. The

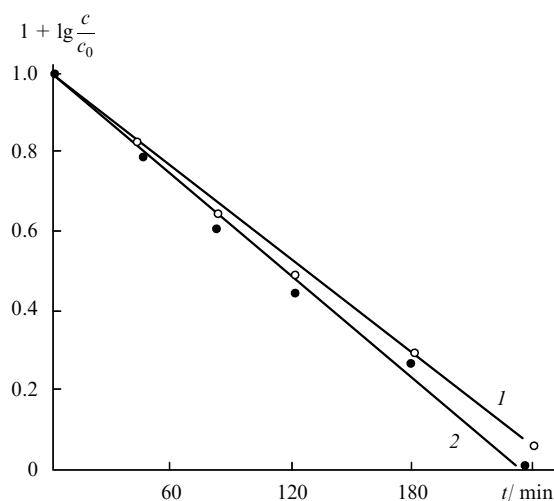


Figure 11. Constants from the curves for the consumption of BP at $c_0 = 0.66 \text{ mol kg}^{-1}$ and a temperature of 371 K in evacuated CTA films in the presence of 0.08 (1) and 0.32 mol kg^{-1} (2) of a methoxyquinoid ionol derivative (3,5-di-*tert*-butyl-1-methyl-1-methoxycyclohexadien-4-one).

concentration of this ether, like those of phenols, appears in the expression for the effective rate constant of the reaction of BP as a parameter. This confirms the fact that the quinoid compound is quickly transformed into the corresponding phenol by a thermofluctuation mechanism.

VII. The mechanism of the initiated chain process involving ionol during the induction period of the oxidation of polyalkenes

The data presented above make it possible to consider the chemical aspect of the inhibited oxidation of polyalkenes during the induction period from a new standpoint. A lot of experimental results and theoretical studies have been accumulated in this field; however, as a rule, they do not go beyond homogeneous reaction models.^{14–16}

One of the two methodological approaches to the solution of this problem is based on the use of initiators that have been tested in liquid-phase reactions.^{15,16} In the case of liquid-phase oxidation, this method makes it possible to determine, using relatively simple experiments, the character and specific features of the influence of a particular inhibitor on the rate of oxygen absorption and on the duration of the induction period, after which the action of the inhibitor ends.

Another approach involves investigation of the inhibited oxidation of a polymer containing no specially added initiator.¹⁴

In this Section, we consider oxidation of polymers in the presence of an initiator added as an admixture; attention is focused on the regularities of the absorption of oxygen during the induction period. The fact that oxygen absorption does occur at a certain rate during the induction period of inhibited oxidation of polyalkenes in the presence of an initiator has been long known; however, it has not yet received any acceptable explanation. Among other reasons, this is due to the fact that the rate of oxygen absorption in this stage is lower than that in the stage of the polymer oxidation itself (after completion of the induction period). In determining the efficiency of inhibitors or the rate of generation of oxidation chains, researchers have believed that it was sufficient to choose conditions under which the rate of the consumption of an inhibitor did not depend on its concentration. It has been assumed that under these conditions, slow absorption of oxygen during the induction period of the polymer oxidation can be neglected.^{15,16,28} Meanwhile, insight into the mechanism of the transformation of alkylphenols with allowance for the specific

features of functioning of the chain-sponge structure in polymers, should aid greatly the refinement of general views on the mechanism of oxidative transformations involving inhibitors.

To construct a kinetic model of the process occurring during the induction period, we used experimental data reported by Chien and Wang,²⁸ who have carried out oxidation of polypropylene, poly(but-1-ene), and poly(4-methylpent-1-ene) (under an oxygen pressure of 1 atm) using dibenzoyl peroxide as the initiator and ionol as the inhibitor. Although the workers did not consider the reason why oxygen is absorbed noticeably during the induction period, they presented, among other results, fairly detailed data on the rate of the absorption of oxygen (V) and the rate of the consumption of ionol (V_i) during this stage of the reaction.

The process of oxidation of these polymers, which are partly crystalline, involved only their amorphous regions and was limited to a very early stage, corresponding to a degree of BP conversion of 0.6% to 2%.

The values $V_i = c_{i0}/t_{\text{ind}}$ (c_{i0} is the initial concentration of ionol and t_{ind} is the induction period) measured in the temperature range between 344 and 378 K, as well as the V values remained constant for the concentrations of BP used up to the instant when the oxidation process sharply accelerated due to exhaustion of ionol.

The workers proved definitely that no chain transformation of BP proceeded under oxidative conditions and found the temperature dependence of the coefficient A

$$A = \frac{c_{i0}}{c_0 [1 - \exp(-k_d t_{\text{ind}})]} \quad (30)$$

Since the discussion was carried out within the framework of a liquid-phase model, they considered A to be a parameter characterising the influence of the inhibitor on the yield of radicals in spontaneous reaction of BP.

However, comparison of the rates of consumption of ionol and oxygen during the induction period makes it possible to give a different interpretation of this coefficient. The results of this comparison are presented in Fig. 12 in which straight lines 1, 2

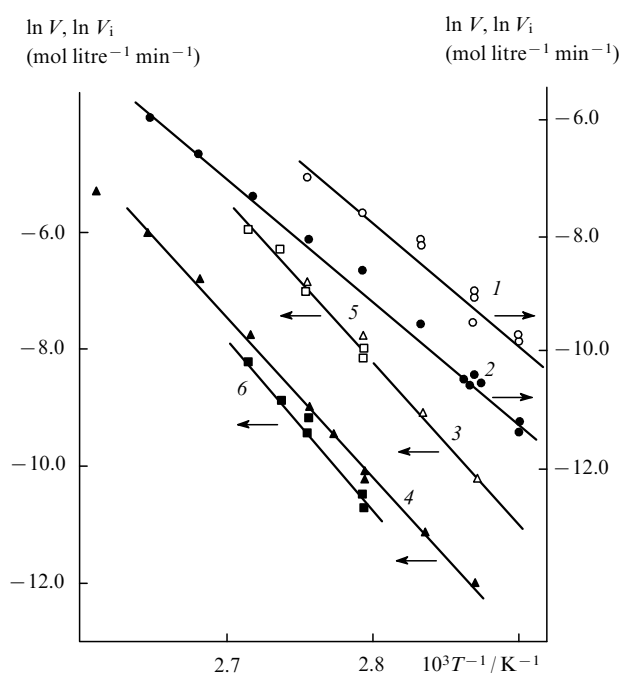


Figure 12. Temperature dependences of the rates of oxygen (1, 3, 5) and ionol (2, 4, 6) consumption during the induction period of oxidation of polypropylene (1, 2), poly(but-1-ene) (3, 4) and poly(4-methylpent-1-ene) (5, 6), initiated by dibenzoyl peroxide.

and 3 plotted on the Arrhenius coordinates refer to the variation of the rate of oxygen absorption, while straight lines 2, 4 and 6 refer to the rate of consumption of ionol. These temperature dependences remain linear as c_{i0} varies from 3.4×10^{-3} to 72.6×10^{-3} mol litre $^{-1}$, which is a consequence of the fact that these rates do not depend on the concentration of ionol. The identical slopes of the straight lines characterising consumption of oxygen and ionol during oxidation of each polymer indicate that the effective activation energies of the two macroscopic processes are identical ($E_i = E_{O_2}$). In the case of PP (straight lines 1 and 2; $c_0 = 0.127$ mol litre $^{-1}$), this energy is equal to 127 kJ mol $^{-1}$, while for polybut-1-ene (straight lines 3 and 4; $c_0 = 0.376$ mol litre $^{-1}$) and for polymethylpentene (straight lines 5 and 6; $c_0 = 0.33$ mol litre $^{-1}$), it is 231.0 kJ mol $^{-1}$. The number of oxygen molecules absorbed per ionol molecule consumed remains constant over the whole temperature range studied. The V/V_i ratios are 3.65, 8.0 and 13.5 for PP, poly(but-1-ene) and poly(4-methylpent-1-ene), respectively.

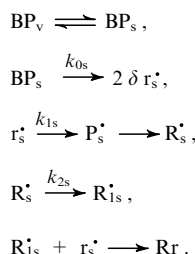
It can be seen that the stoichiometric V/V_i ratio depends on the chemical structure of the polymer and can be so great that this cannot be due to oxidation of only the ionol added. Therefore, the process occurring during the induction period can be regarded as initiated chain co-oxidation of the alkylphenol and the polymer. In this case, formula (30) characterises variation of the amount of ionol consumed in the chains of its co-oxidation with the polymer per BP molecule decomposed spontaneously rather than the influence of ionol and temperature on the emergence of radicals from the 'cage' of spontaneously decomposing BP.

According to Ref. 28, the rate constant of the spontaneous decomposition of BP k_d is $8.4 \times 10^{13} \exp(-124\,650/RT)$ s $^{-1}$ in PP and poly(but-1-ene) and $7 \times 10^{13} \exp(-123\,000/RT)$ s $^{-1}$ in poly(4-methylpent-1-ene). The activation energy for the decomposition of BP ($E_d = 123$ to 125 kJ mol $^{-1}$) during the oxidation of these polymers is much less than the activation energy for their co-oxidation with ionol (172 – 231 kJ mol $^{-1}$). Therefore, the temperature dependence of A found previously,²⁸ which corresponded to an extremely low degree of BP decomposition (from 0.6% to 2% over the time t_{ind}), characterises the ratio between the rates

$$A = \frac{c_{i0}}{c_0 [1 - \exp(-k_d t_{ind})]} = \frac{c_{i0}}{c_0 k_d t_{ind}} = \frac{V_i}{V_{d0}},$$

where $V_i = c_{i0}/t_{ind}$ and $V_{d0} = k_d c_0$.

The structural-kinetic model of the co-oxidation can be constructed quite easily taking into account considerations presented in the above Sections and also the facts that the systems in question contain initially no hydroperoxide, able to decompose in v-zones of the chain-sponge matrix by the mechanism of fluctuational excitation of v-micropores, and that BP molecules decompose to give radicals in the s-zones

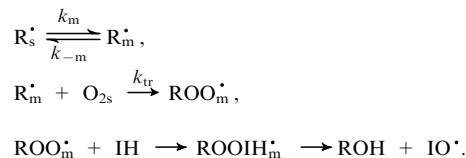


This s-scheme differs from that considered above by the presence of a stage of recombination of s-benzoyloxy radicals with $\text{R}_{1s}^{\bullet}$ macroradicals. This recombination was discovered in a study of the material balance of phenyl-containing compounds in the reaction between BP and PP.³⁴

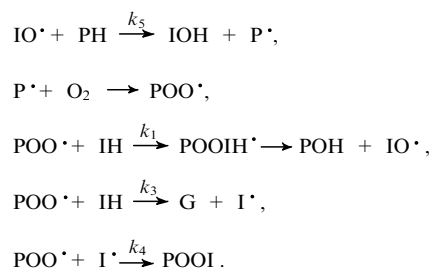
According to the s-scheme suggested, the steady-state concentration of radicals that accomplish the interzone s,v-transfer of free valence is equal to

$$[\text{R}_s^{\bullet}] = \frac{\delta k_{0s} c_s}{k_{2s}}.$$

The acts of s,v-transfer themselves should occur with a low frequency, having no influence on $[\text{R}_s^{\bullet}]$ (this is ensured by the rigidity of the chain-sponge framework):



The quinoid alkoxy radicals, which appear in this way in v-zones, initiate chain oxidation of macromolecules, ionol being also involved in this process:



Here we follow the numbering of rate constants k_1 , k_3 and k_4 accepted in the previous Section. It is suggested that the steps of ionol regeneration and consumption, characterised by the rate constants for the 'latent radical' stages in the transformation of the alcohol IOH (k_{1f} , k_{-1f} , k_{2f} and k_{3f}), are also retained in this case.

Within the framework of the present heterophase scheme, the fact that the rates of generation and termination of reaction v-chains are equal is represented by the following expression

$$V_{tr} = \frac{k_{tr} k_m \delta k_{0s} c_s [\text{O}_{2s}]}{k_{2s} (k_{-m} + k_{tr} [\text{O}_{2s}])} = 2 k_3 [\text{POO}^{\bullet}] [\text{IH}]. \quad (31)$$

Assuming that these chains are sufficiently long, which permits the use of the approximate equality

$$k_5 [\text{IO}^{\bullet}] [\text{PH}] \approx k_1 [\text{POO}^{\bullet}] [\text{IH}]$$

we obtain the steady-state concentration condition for the quinoid alcohol

$$k_1 [\text{POO}^{\bullet}] [\text{IH}] = \frac{k_{1f} [\text{IOH}] [\text{PH}] (k_{2f} + k_{3f})}{k_{-1f} + k_{2f} + k_{3f}}.$$

Now we substitute the product $[\text{IOH}] [\text{PH}]$, found from the above relation, in the equation for the rate of ionol consumption

$$\begin{aligned} -\frac{dc_i}{dt} &= k_1 [\text{POO}^{\bullet}] [\text{IH}] + k_3 [\text{POO}^{\bullet}] [\text{IH}] - k_{2f} [\{\text{I}^{\bullet} + \text{HO}^{\bullet} + \text{PH}\}] = \\ &= (k_1 + k_3) [\text{POO}^{\bullet}] [\text{IH}] - \frac{k_{2f} k_{1f} [\text{IOH}] [\text{PH}]}{k_{-1f} + k_{2f} + k_{3f}} = \\ &= (k_1 + k_3) [\text{POO}^{\bullet}] [\text{IH}] - (1 - \beta) k_1 [\text{POO}^{\bullet}] [\text{IH}]. \end{aligned}$$

Then we neglect the consumption of ionol in the chain termination steps (with rate constant k_3) and find, using formula (31), the $[\text{POO}^{\bullet}] [\text{IH}]$ product for a system saturated with oxygen ($k_{-m} \ll k_{tr} [\text{O}_{2s}]$); thus

$$V_i = -\frac{dc_i}{dt} = \frac{0.5 k_{3f} k_1 k_m \delta k_{0s} c_s}{(k_{2f} + k_{3f}) k_3 k_{2s}}.$$

Taking into account the interzone equilibrium of BP [Eqn (1)], we finally obtain

$$V_i = \beta k_i c,$$

where k_i is the complex constant and $\beta = k_{3f} / (k_{2f} + k_{3f})$.

From the same heterophase scheme subject to the conditions listed above, we obtain the following expression for the rate of oxygen consumption

$$\begin{aligned} V = -\frac{d[O_2]}{dt} &= k_5 [IO^\cdot] [PH] = k_1 [POO^\cdot] [IH] = \\ &= \frac{0.5 k_1 k_m \delta k_{0s} c_s}{k_3 k_{2s}} = k_i c. \end{aligned}$$

Thus, it can be seen that the theory of heterophase transformation in a system based on a polymer containing relatively large amounts of alkylphenol and oxygen in addition to an initiator leads to the rates of the consumption of inhibitor (V_i) and oxygen (V), which do not depend on their concentrations and are directly proportional to one another:

$$\frac{V}{V_i} = \frac{1}{\beta} = \frac{k_{2f} + k_{3f}}{k_{3f}}.$$

This implies that the fact that V is substantially greater than V_i is associated with regeneration of alkylphenol. Thus, the observed increase in the V/V_i ratio from 3.65 to 13.5 means that the efficiency of regeneration (β^{-1}) increases in the sequence: polypropylene > poly(but-1-ene) > polymethylpentene and is probably a result of the increase in the number of reactive hydrogen atoms on the surfaces of thermofluotually excited v-micropores. The larger is the number of these hydrogen atoms surrounded by arising $HO^\cdot$ and $I^\cdot$ radicals, the lower is the probability of mutual disproportionation of radicals and the higher is the probability of dehydrogenation of macromolecules by the 'latent radical' mechanism.

It should be specially emphasised that regeneration of alkylphenol is exactly an 'intracage' latent radical reaction occurring over the life span of a micropore grown to the required size. The emergence of radicals from such a micropore into the bulk of v-zones of the chain sponge occurs at a negligibly low rate and has no influence on the steady-state concentrations of v-radicals. In this connection, it is also noteworthy that the temperature dependence of

$$A = \frac{c_{i0}}{c_0 [1 - \exp(-k_d t_{ind})]}$$

reported previously²⁸ is not associated with the process, considered in the same study, of thermally activated diffusional insertion of ionol into a 'cage' formed upon spontaneous decomposition of the initiator. In conformity with the concept of chain co-oxidation of ionol and polyalkene, this dependence characterises the stoichiometry of chain co-oxidation. The reaction model proposed by us reveals the structure of coefficient A , which is described by the equation

$$A = \frac{V_i}{V_{d0}} = \frac{0.5 \delta \beta k_1 k_m}{k_3 k_{2s}}.$$

The coefficient β appearing in this formula depends only slightly if at all on the temperature, which follows from the fact that the E_{O_2} and E_i values are equal for all the polymers studied.²⁸ Therefore, the main contribution to the temperature dependence of A is made by the steps of migration of the terminal macroradicals $R_s^\cdot$ from the framework walls into the bulk of s-micropores (the rate constant k_m). The size of the corresponding mediator fragment

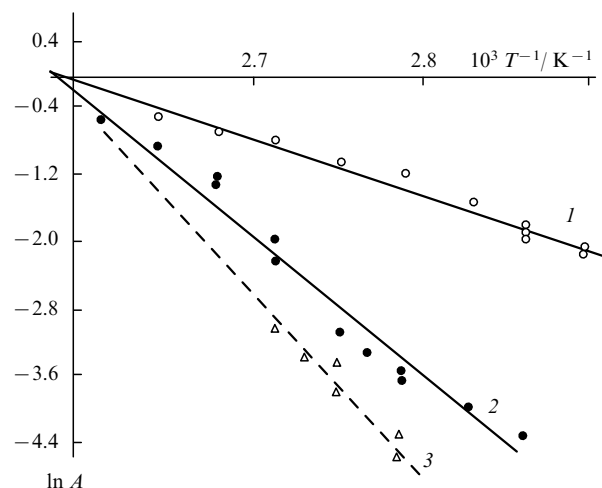


Figure 13. Temperature dependences of coefficients A in Arrhenius coordinates for polypropylene (1), poly(but-1-ene) (2) and poly(4-methylpent-1-ene) (3).

($R_s^\cdot \rightleftharpoons R_m^\cdot$) increases in the order: polypropylene < poly(but-1-ene) < polymethylpentene; therefore it is natural to expect that the restrictions to this migration will also increase in the same sequence. The temperature dependences of coefficients A plotted on the Arrhenius coordinates indicate that the activation energy E_A increases from 50 kJ mol⁻¹ for PP to 128 kJ mol⁻¹ for poly(but-1-ene) and to even a larger value for poly(4-methylpent-1-ene) (Fig. 13).

In the absence of an adequate theoretical base, Chien and Wang²⁸ could not construct the plots presented in Fig. 13. Meanwhile, it follows from these plots that in the case of PP, the parameter A is equal to 1 at 388 K, while at 405 K, it exceeds 2 ($\ln 2 = 0.693$). It is clear that dissociation of a BP molecule cannot yield more than two free radicals; thus, an A value, larger than 2, denudes of its physical meaning the suggestion made in Ref. 28 that the coefficient A characterises the output of radicals in the steps of generation of oxidation chains.

Since the physical sense of the coefficient A has changed, the interpretation of the coefficient f , determined by the procedures used for homogeneous reactions, should also change. When the inhibitor method is used, the coefficient f is calculated from the formula

$$f = \frac{W_{i0}}{V_i} = \frac{2 \delta V_{d0}}{V_i},$$

where W_{i0} is the rate of homogeneous generation of radicals, and δ is a coefficient characterising the output of radicals in the steps of dissociation of the initiator. In this case, the parameter f characterises the number of oxidative chains terminated by one molecule of the inhibitor. At the same time, by definition, f is inversely proportional to the parameter A :

$$f \sim \frac{V_{d0}}{V_i} = \frac{1}{A}.$$

Thus, as applied to polymers, this coefficient is also a particular characteristic of the chain co-oxidation of the inhibitor with the polymer. The instant when the inhibitor in the polymer is exhausted, which is detected by a sharp increase in the rate of oxygen absorption, corresponds to the end of the co-oxidation period and to the transition to the stage of oxidation of the polymer itself.

The application of the homogeneous reaction model to the oxidation of a polymer during the induction period gives rise to some inconsistencies. Let us consider, for example, a study³⁵

dealing with oxidation of PP in the presence of ionol with dicumyl peroxide as the initiator ($P_{O_2} = 1 \text{ atm}$, $T = 388 \text{ K}$). In this study, the coefficient f was found to be

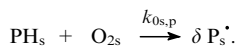
$$f = \frac{W_i}{V_i} = 1$$

(W_i is the constant rate of radical generation found by the inhibitor method, and V_i is the rate of ionol consumption). Since at a constant W_i , the inhibitor was consumed at an invariant rate, it was concluded³⁵ that all the chains were terminated at the inhibitor and that there were no side reactions leading to its consumption; and the equality $f = 1$ corresponded to one oxidation chain terminated at one ionol molecule (recall that according to the data presented in Fig. 13, $A = 1$ at $T = 388 \text{ K}$). However, the workers had to note that the f value obtained differed from the value $f = 2$, typical of the liquid phase, and they also presented a number of facts proving that bimolecular destruction of the ionol-based phenoxyl radicals ($I^\bullet + I^\bullet \rightarrow \text{products}$) occurred in the PP matrix. However, the data discussed in Section VI indicate that this mechanism is by no means consistent with the actual kinetics of the destruction of phenoxyl radicals.

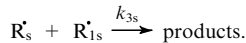
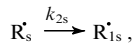
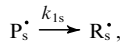
VIII. Chain co-oxidation of alkylphenol with polyalkene in the absence of an initiator

We shall analyse the co-oxidation occurring in the absence of an initiator using the v-scheme considered in the previous Section and taking into account the fact that the rate of radical generation in v-zones is negligibly small. Under these conditions, initiation can occur in s-zones, which serve as a heterophase source of radicals, *via* either direct oxidation of polymer s-chains or oxidation of molecules of an inhibitor if they are sufficiently reactive.

To consider the former possibility, let us examine the s-scheme, which previously has made it possible to give kinetic description for the initial stage of autooxidation of PP in the absence of an initiator and an inhibitor.^{4,25} According to this scheme, radicals are generated in supermicropores of chain-sponge s-zones upon the interaction of the CH bonds in the polymer chains with the oxygen adsorbed on the walls of s-micropores.



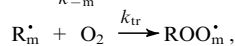
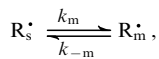
Subsequent transformations of s-macroradicals occur in the same way as was described in Sections II and V



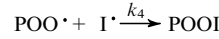
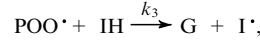
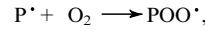
The expression for the concentration of mediator radicals, which follows from this scheme, has the form

$$[R_s^\bullet] = \frac{\delta k_{0s,p}}{2 k_{2s}} [PH_s] [O_{2s}]$$

whereas the s,v-translation of valence, involving these radicals, is described by the scheme



The scheme for the reaction v-chains of the co-oxidation of alkylphenol and polymer



is retained without changes. So is the scheme of the latent radical transformations of the quinoid alcohol IOH, which ensure partial regeneration of the initial phenol.

This combination of s- and v-schemes indicates that the macroradicals occurring within individual zones are non-equivalent with respect to oxidation and interaction with the inhibitor: in supermicropores, the rates of these processes are low, whereas in v-zones, on the contrary, they are high. This selectivity, which is associated with the predominant accumulation of low-molecular-weight compounds (including oxygen and the inhibitor) in the grains of sponge micelles filled with narrow micropores, is obviously a general phenomenon.^{1-6,11-13,25} An example of this non-equivalent behaviour has been considered in the description of the transformations of ionol in the s-chains of initiated destruction of macromolecules and in the v-chains of arylation of CTA and PC (Section II). A number of similar facts have been reported. For example, it is quite characteristic that the number of polymer chains cleaved per unit time in the oxidation of molten polystyrene at 473 K ($P_{O_2} = 150 \text{ mm Hg}$) in the presence of bisphenol 2246 as an inhibitor remains virtually unchanged over a period of 26 h.^{36,37} This phenomenon is observed during the induction period if the concentration of the inhibitor is high; in the case of a low inhibitor concentration ($c_i \rightarrow 0$), it is observed after the induction period has been completed. In the oxidation of rubber in the presence of ionol³⁸ and in the oxidation of PP in the presence of bisphenol 2246 (437 K, $P_{O_2} = 300 \text{ mm Hg}$),³⁰ the concentration of inhibitor also has no influence on the rate of the polymer destruction during the induction period.

Thus, the heterophase scheme suggested for the non-initiated co-oxidation of alkylphenol and the polymer conforms to the general features observed for the induction period of the process and takes into account the specific features of co-oxidation in a heterogeneous chain-sponge micellar matrix considered previously.

By applying the condition of steady-state concentration of radicals to each unit of the overall scheme of the process considered, it is easy to obtain an expression for the rate of the s,v-transfer of free valence

$$V_{tr} = k_{tr} [R_m^\bullet] [O_{2s}] = \frac{k_{tr} k_m \delta k_{0s,p} [PH_s] [O_{2s}]^2}{k_{-m} + k_{tr} [O_{2s}]}$$

If the polymer has been saturated with oxygen ($k_{-m} \ll k_{tr} [O_{2s}]$), this expression assumes the following form

$$V_{tr} = \frac{\delta k_{0s,p} k_m [PH_s] [O_{2s}]}{2 k_{2s}} \quad (32)$$

The V_{tr} value, which is simultaneously the rate of generation of the reaction v-chains, is equal to the rate of their termination.

$$V_{tr} = 2 k_3 [POO^\bullet] [IH]$$

Under the conditions considered, the rate of consumption of alkylphenol does not depend on its concentration but depends on the oxygen pressure:

$$V_i = -\frac{dc_i}{dt} = (k_1 + k_3) [POO^\bullet] [IH] - (1 - \beta) k_1 [POO^\bullet] [IH] \approx$$

$$\begin{aligned} \approx \beta k_1 [\text{POO}'] [\text{IH}] &= \frac{\beta k_1 V_{\text{tr}}}{k_3} = \\ &= \frac{\beta k_1 \delta k_{0s,p} k_m}{4 k_3 k_{2s}} [\text{PH}_s] [\text{O}_{2s}] = \beta k_{i,p} P_{\text{O}_2} \end{aligned} \quad (33)$$

Here $[\text{O}_{2s}] = K_{\text{O}_2} [\text{O}_{2v}] = K_{\text{O}_2} \gamma P_{\text{O}_2}$, where K_{O_2} is the equilibrium constant for the oxygen exchange between the zones, γ is the Henry constant, $\beta = k_{3f}/(k_{2f} + k_{3f})$ is the efficiency of the consumption of quinoid alcohol in the steps of regeneration of phenol (see Sections VI and VII), and $k_{i,p}$ is the complex constant.

According to this scheme, the rate of oxygen absorption

$$V = -\frac{d[\text{O}_2]}{dt} \approx k_5 [\text{IO}'] [\text{PH}] = k_1 [\text{POO}'] [\text{IH}] = k_{i,p} P_{\text{O}_2}$$

exceeds the rate of the inhibitor consumption and also does not depend on its concentration c_i .

It is these regularities that have been established back in early studies dealing with the mechanism of antioxidative stabilisation with phenols, which have been regarded as weak inhibitors. Processes involving inhibitors of this type are characterised by an approximately zero order with respect to the inhibitor, the first order with respect to oxygen, and the linear dependence of the duration of the induction period on the inhibitor concentration. The following antioxidants were studied: 2,6-bis(1,1-dimethylhexyl)-4-methylphenol (at 473 K and at $P_{\text{O}_2} = 300$ mm Hg, the value of t_{ind} increased linearly from 9.5 min at $c_i = 0$ to 373 min at $c_i = 0.20$ mol kg⁻¹),^{39,40} 2,4,6-tri-*tert*-butylphenol (the effective activation energy for the consumption of phenol in the 453–473 K range: $E_i = 151$ kJ mol⁻¹),⁴¹ 2,6-di-*tert*-butyl-4-phenylphenol ($E_i = 126$ kJ mol⁻¹),⁴¹ and a bis-phenol with spatially separated OH groups — 4,4'-methylenebis(2,6-di-*tert*-butylphenol) (the t_{ind} value increased linearly from 9.5 min at $c_i = 0$ to 250 min at $c_i = 0.025$ mol kg⁻¹).⁴¹

One more feature peculiar to the phenols listed above is that their consumption is not accompanied by the formation of water; the appearance of water becomes noticeable only at the very end of the induction period. This important fact indicates that the rates of decomposition of peroxy radicals (with evolution of OH[•]) and of the polymeric hydroperoxide formed in small amounts are negligibly small. The fact that the rates of consumption of oxygen and inhibitor remain constant over the whole induction period also implies that hydroperoxide scarcely makes any contribution to the radical generation at the stage of co-oxidation of the polymer and phenol.⁴²

The heterophase scheme accepted by us does not include reactions of decomposition of POO[•] radicals or hydroperoxide groups; this reflects the fact that the concentration of peroxy radicals sharply decreases when the polymer contains even a minor amount of an inhibitor.

Additional evidence for the chain mechanism of the co-oxidation of polyalkenes and alkylphenols is provided by the substantial deceleration of this process in the presence of dialkyl sulfides.

1. The mechanism of co-oxidation inhibited by dialkyl sulfide

Analysis of the characteristic features of transformations of antioxidants in the polymer-chain zones of sponge micelles causes one to consider the problem of the mechanism of joint action of phenolic antioxidants and dialkyl sulfides. It is known that the latter do not possess any substantial inhibitory activity but extend markedly the induction period in the co-oxidation of a polymer with a 'weak' phenol and change the kinetics of the phenol consumption.^{41,43}

The reasons for the non-additive influence of phenol and dialkyl sulfide have been considered in the literature in terms of the concept of non-radical decomposition of a hydroperoxide by a dialkyl sulfide. It is believed that dialkyl sulfide destroys hydroperoxide without formation of free radicals and thus decreases

dramatically the rate of degenerate branching of oxidation chains, the probability of which during the induction period in the presence of a 'weak' phenol is thought to be relatively high. As shown above, hydroperoxide can hardly act as a branching agent at the stage of co-oxidation, if for no other reason than its fairly low concentration. However, even in the samples in which hydroperoxide has been specially accumulated prior to the reaction, the branching factor of oxidation chains in the presence of alkylphenol is equal to zero (Sections V and VI), and the transformation reduces only to oxidative chain decomposition of hydroperoxide.

Thus, the question of the mechanism of direct interaction of dialkyl sulfide and hydroperoxide, which has not yet been ultimately resolved due to its complexity,¹⁴ becomes a separate problem. It is significant for us that dialkyl sulfide, which is not an inhibitor for the polymer oxidation itself, inhibits its co-oxidation of alkylphenol. In other words, dialkyl sulfide acts as if it extended the period during which alkylphenol is efficient. This is indicated, for example, by the character of kinetic curves for the consumption of 2,6-bis(1,1-dimethylhexyl)-4-methylphenol and bisphenol 2246 obtained for oxidation at 473 K ($P_{\text{O}_2} = 300$ mm Hg).^{14,43} It can be seen from Fig. 14 that the rates of consumption of mono-phenol (the initial concentration was 0.16 mol kg⁻¹) and bisphenol (the initial concentration was 0.08 mol kg⁻¹) in the presence of 0.08 mol kg⁻¹ of a sulfide are lower than those in the absence of the sulfide. This is observed even at the very beginning of the reaction when a change in the yield of radicals in the steps of hydroperoxide decomposition under the influence of both phenol and sulfide is out of the question. As has already been noted, influence of this sort is not manifested even at high concentrations of hydroperoxide (Sections V and VI).

In addition, we mention important results,³⁰ according to which in the oxidation of molten PP (473 K, $P_{\text{O}_2} = 300$ mm Hg), the rate of evolution of propene remains constant over 100 min in the induction period; this rate is the same in the presence of 0.025

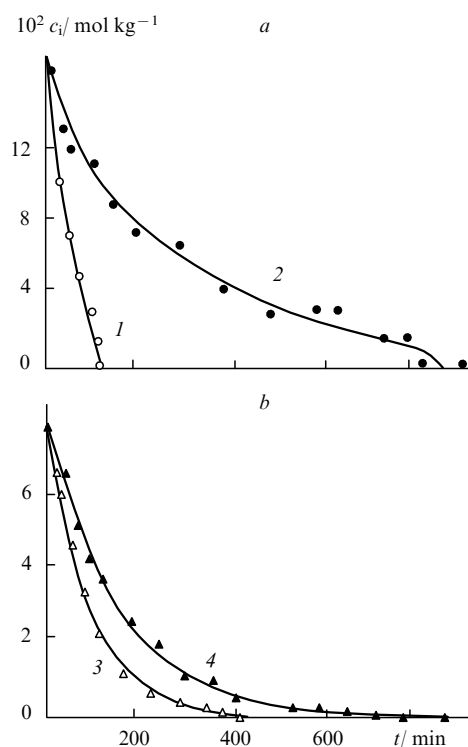
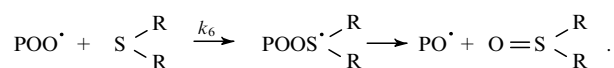


Figure 14. Curves for the consumption of 2,6-bis(1,1-dimethylhexyl)-4-methylphenol (a) and 2,2'-methylenebis(6-*tert*-butyl-4-methylphenol) (b) during the induction period of the oxidation of polypropylene (473 K, $P_2 = 300$ mm Hg) in the absence (1, 3) and in the presence (2, 4) of 0.08 mol kg⁻¹ of didecyl sulfide.

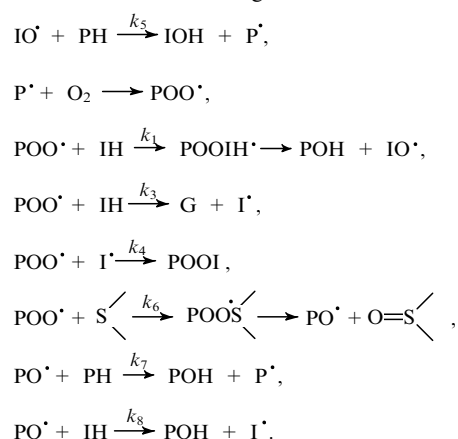
or 0.05 mol kg⁻¹ of bisphenol 2246; it also does not change when 0.08 mol kg⁻¹ of didecyl sulfide or dilauryl thiodipropionate are introduced in the reaction mixture. In other words, under these conditions, the concentration of depolymerising terminal macro-radicals remains constant over a period of 100 min, and the process of degenerate branching involving hydroperoxide and phenol can be neglected.

At the same time, gas-chromatographic analysis has shown that the introduction of dialkyl sulfides in the PP being oxidised leads to a substantial increase in the yield of ethylene,³⁰ which indicates that sulfides interact with polymeric peroxy radicals. When dialkyl sulfides are involved in co-oxidation with PP, they do not extend markedly the induction period. However, in the presence of a 'weak' phenol, a synergistic effect is manifested, and the induction period can become much longer. The mechanism of this phenomenon can be understood by taking into account the known³⁰ fact that dialkyl sulfides react with peroxy radicals; this leads to a decrease in the concentration of peroxy radicals, which induce the chain consumption of alkylphenol.

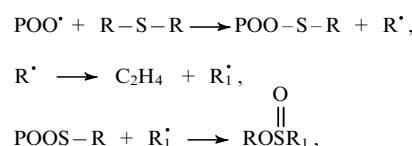
For this purpose, dialkyl sulfide should ensure the conversion of peroxy into a polymeric alkoxy, which then reacts predominantly with the inhibitor:



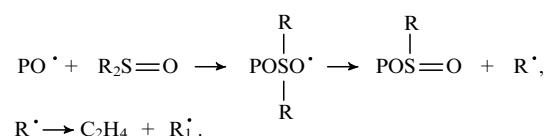
With allowance for the assumptions made, the scheme for the reaction v-chains of co-oxidation of the polymer, phenol, and sulfide assumes the following form:



In the absence of phenol, the role of dialkyl sulfide reduces to its consumption with the rate constant k_6 in the transformation of peroxy radicals into alkoxy radicals, which then produce oxidisable alkyl radicals $\text{P}^\bullet$ in a stage with the constant k_7 . This results in the reduction of $\text{POO}^\bullet$. The overall sequence of reactions does not lead to a change in the concentration of peroxy radicals; therefore, the consumption of dialkyl sulfide has no influence on the rate of oxidation of the polymer. The transformation of sulfide yielding ethylene, which either follows a replacement mechanism³⁰



or occurs as a reaction of the alkoxy radical formed with sulfoxide



is not shown in the scheme. These processes seem to be energetically and sterically less favourable than the stage characterised by constant k_6 , which involves rupture of the weak peroxide bond and formation of a strong S—O bond. Therefore, the formation of ethylene can be regarded as a side process. Besides, it does not influence the kinetic picture of the co-oxidation with phenol, because $\text{R}_1^\bullet$ radicals are oxidised to peroxy radicals, which qualitatively do not differ from polymeric peroxy radicals.

The co-oxidation v-scheme under consideration includes a stage in which phenol interacts with $\text{PO}^\bullet$ radicals and terminates the reaction chains involving dialkyl sulfide. Thus, the sulfide assumes an inhibitory function, which was lacking initially.

However, when the concentration of phenol is sufficiently high, the oxidative chains predominate again due to an increase in the rates of reactions characterised by constants k_1 and k_5 . This ensures a co-oxidation route independent of the presence of dialkyl sulfide.

By applying the condition of steady-state radical concentration to the v-scheme described above and resorting to the above assumption that regeneration of phenol occurs by a latent-radical mechanism, we can obtain quite easily an expression for the rate of consumption of the inhibitor

$$\begin{aligned} V_i &= -\frac{dc_i}{dt} \approx \beta k_1 [\text{POO}^\bullet] c_i = \\ &= \frac{0.5 \beta k_1 c_i V_{tr}}{k_3 c_i + k_6 k_8 c_i c_s / (k_7 [\text{PH}] + k_8 c_i)}, \end{aligned}$$

where c_s is the concentration of dialkyl sulfide. This equation can be brought to identical forms at opposite concentration ratios

$$\frac{c_i}{c_s} \ll 1 \text{ and } \frac{c_i}{c_s} \gg 1.$$

In fact, when the concentration c_i is low, so that the inequality $k_7 [\text{PH}] \gg k_8 c_i$ holds, the second term in the denominator of the main fraction in the expression for V_i can be neglected. Conversely, if the concentration c_i is high, then $k_7 [\text{PH}] < k_8 c_i$; but the inequality $k_3 c_i > k_6 c_s$ is also valid. The final results are identical in both cases

$$V_i = \frac{0.5 \beta k_1 V_{tr}}{k_3},$$

i.e. dialkyl sulfide has no influence on the rate of the process.

However, when the ratio of concentrations is intermediate

$$\frac{c_i}{c_s} \approx 1$$

and the inequality $k_7 [\text{PH}] < k_8 c_i$ holds in combination with $k_3 c_i < k_6 c_s$, then the expression for the rate of consumption of the inhibitor assumes the following form

$$V_i = \frac{0.5 \beta k_1 c_i V_{tr}}{k_6 c_s}.$$

Consequently, within a certain time interval, the process is first order with respect to phenol, which is in agreement with Eqn (32) describing the rate of translation of radicals V_{tr} to the v-zones of sponge micelles. The rate of consumption of the 'weak' phenol decreases, since the inhibitory activity of dialkyl sulfide induced by phenol is fully manifested under these conditions. Comparison of dependences 1 and 2 in Fig. 14 indicates that the kinetic law for the consumption of the inhibitor has actually changed in agreement with the theoretical prediction, which follows from the heterophase model of the induction period of the process.

The influence of dialkyl sulfides on the duration of the induction period of the oxidation of polyalkenes mixed with bisphenol 2246, which is considered to be a strong inhibitor,¹⁴ is less pronounced. The deceleration of consumption of bisphenol is also manifested to a lesser degree than that for a weak phenol (Fig. 14, curves 3 and 4). Molecules of bisphenol 2246 differ from molecules of 'weak' phenols, on the one hand, by less efficient shielding of the OH groups by the neighbouring alkyl substituents (and, hence, their higher accessibility to attacking radicals and to oxygen molecules) and, on the other hand, by specific mutual arrangement of the benzene nuclei (see Section III). For these reasons, direct oxidation of bisphenol 2246 occurring in s-zones of the polymer-chain sponge to yield radicals is facilitated (Scheme 1).

$$\text{HIIH}_s + \text{O}_{2s} \xrightarrow{k_{0s,ii}} \text{[Intermediate 1]} \rightarrow \text{[Intermediate 2]} \rightarrow \text{[Intermediate 3]}$$

$$\text{[Intermediate 3]} \xrightarrow{\text{HIIH}_s} \text{[Intermediate 4]}$$

$$\text{[Intermediate 4]} \rightarrow \text{HIIOOH}_s \text{ (intramolecular disproportionation)}$$

$$\text{HIIOOH}_s \rightarrow \text{[Intermediate 5]} + \text{H}_2\text{O}$$

$$\cdot\text{HIO}_s + \text{PH}_s \rightarrow \cdot\text{HIOH} + \text{P}'_s$$

$$\text{P}_s \xrightarrow{k_{1s}} \text{R}'_s$$

$$\text{R}'_s \xrightarrow{k_{2s}} \text{R}'_{1s}$$

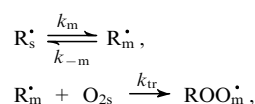
$$\text{R}'_s + \text{R}'_{1s} \xrightarrow{k_{3s}} \text{products}$$

$$\text{R}'_{1s} + \cdot\text{HIOH}_s \rightarrow \text{R}^= + \text{HIIOH}_s$$

In conformity with the s_{ii}-scheme, the steady-state concentration of mediator radicals, responsible for the interzone s,v-transfer of radicals, is

$$[\text{R}_s\cdot] = \frac{\lambda c_{\text{ii}} P_{\text{O}_2}}{2k_{2s}},$$

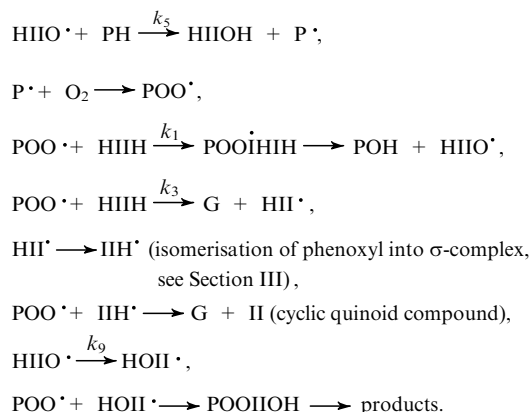
The transfer of free valence from s-zones into v-zones, as in the case of phenols considered previously, occurs *via* intermediate formation of active quinoid alkoxy radicals



It is known^{14, 40, 44} that in the presence of bisphenol 2246, the induction period (more precisely, the period of co-oxidation) is much longer, and the influence of dialkyl sulfides is substantially less pronounced than in the case of 'weak' monophenols. Both of these effects may be due to the specific structure of the bisphenol molecule, which ensures large probability of isomerisation of active alkoxyl into inactive phenoxyl *via* an intermediate radical of the benzyl type (Scheme 2).

$$\begin{aligned} \text{HII}\dot{\text{O}}_{\text{m}} &\xrightarrow{k'_{\text{tr}}} \text{HII}\dot{\text{O}} \cdot, \\ \text{HII}\dot{\text{O}}_{\text{m}} &\xrightarrow{k_{\text{is}}} \text{HOII} \cdot \end{aligned}$$
$$V_{\text{tr}} = k'_{\text{tr}} [\text{HII} \text{O}_m] = \frac{\delta_{\text{ii}}, \lambda c_{\text{ii}} P_{\text{O}_2}}{2k_{\gamma_s}} = \frac{\delta_{\text{ii}}}{2k_{\gamma_s}}, \quad (34)$$
$$\delta_{ii} = \frac{k_m k'_{tr}}{k'_{tr} + k_{is}} < k_m.$$

A similar isomerisation of phenoxy radicals makes a contribution to the termination of co-oxidation chains in v-zones of the polymer:



It is assumed that here, as in the case of monophenols, partial regeneration of the initial bisphenol from the quinoid alcohol HIIOH occurs by the latent radical mechanism.

Since an additional route for the termination of the reaction v-chains exists, this process occurs at a lower concentration of the peroxy radicals POO[•]. This concentration can be found from the condition of equality of the rates of v-chain generation and termination:

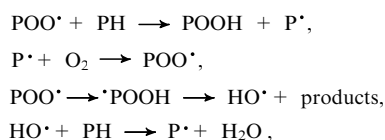
$$\begin{aligned}
V_{\text{tr}} &= 2k_3[\text{POO}^\bullet]c_{\text{ii}} + 2k_9[\text{HIIO}^\bullet] = \\
&= 2k_3[\text{POO}^\bullet]c_{\text{ii}} + \frac{2k_1k_9[\text{POO}^\bullet]c_{\text{ii}}}{k_5[\text{PH}]}.
\end{aligned}$$

For this reason, and also due to the fact that radicals lose their reactivity during s,v-translation [in Eqn (34), $\delta_{\text{ii}} < k_{\text{m}}$], the rate of consumption of bisphenol becomes much lower than that of monophenols [Eqn (33)].

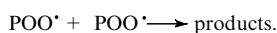
$$V_{\text{ii}} = -\frac{dc_{\text{ii}}}{dt} \approx \beta k_1[\text{POO}^\bullet]c_{\text{ii}} = \frac{\beta k_1 \delta_{\text{ii}} \lambda c_{\text{ii}} P_{\text{O}_2}}{(2k_3 + 2k_1k_9/k_5[\text{PH}])2k_{2s}}.$$

Simultaneously, the induction period of the polymer oxidation becomes longer, and the opportunity for the synergistic action of a dialkyl sulfide decreases.

Thus, within the framework of the heterophase model, the induction period is distinguished as a macroscopic stage involving chain co-oxidation of the inhibitor and the polymer. At this stage, alkylphenol actively participates in the chain process and is mostly consumed in the steps of propagation of co-oxidation chains rather than in the steps of termination of oxidation chains. This period is finished when the concentration of the inhibitor decreases and the concentration of peroxy radicals increases to a degree at which the rate of oxygen absorption is determined only by the steps of oxidation of the polymer itself^{4–6, 25}



and by bimolecular chain termination steps



The fact that both in the presence of an inhibitor and after its complete exhaustion the oxidation process does not switch to a regime with non-degenerate (non-stationary) branchings of reaction chains is of primary importance. The transition from co-oxidation to the oxidation of the polymer itself occurs when the condition of steady-state concentration of peroxy radicals is fulfilled. This requirement is also retained when the regime of co-oxidation changes from the zero order to an apparent first order with respect to phenol following the introduction of dialkyl sulfide into the system.

It should be noted that the extension of the induction period, which accompanies the change in the regime, is often manifested quite clearly in the $t_{\text{ind}}(c_{\text{i}0})$ plots, the concentration of phenol at the inflection point in the curve being interpreted as the critical concentration corresponding to the transition from a non-stationary branched chain process to stationary oxidation.¹⁴ The fact that the stage with non-stationary branching does exist was confirmed¹⁴ by the observation that at a relatively high temperature (~ 473 K), the lifetime of hydroperoxide is limited to several seconds. However, the chain heterophase mechanism of anaerobic decomposition of hydroperoxide was not taken into account.

In the absence of oxygen, decomposition of hydroperoxide follows a chain mechanism, the contribution of spontaneous decomposition to the overall hydroperoxide consumption, as has been shown in Section IV, being negligibly small.^{5, 6} Despite the fact that according to Eqn (18), the life span of hydroperoxide within s-micropores at $T \approx 473$ K is tens of seconds, the lifetime of the main bulk of hydroperoxide in the dissociated state, which is localised in the narrow micropores of v-zones of the chain sponge is much higher. For example, it is remarkable that in the absence of oxygen at 453 K, polystyrene hydroperoxide decomposes by half over a period of 12–15 min, while under conditions of oxidation of molten polystyrene[†] at 473 or 453 K it is accumulated, together with other products, for 30 or 100 min, respectively⁴⁵ and does not decompose noticeably until it begins to react with accumulated products of the polymer oxidation. After that, the accumulation of hydroperoxide ceases, and its concentration decreases.

The data considered in the present and previous Sections indicate that the explanation of the ‘critical’ concentration of phenols proposed previously¹⁴ was inadequate. In terms of our structural-kinetic reaction model, the inflection in the $t_{\text{ind}}(c_{\text{i}0})$ curve caused by the presence of dialkyl sulfide is due to the decrease in the rate of consumption of phenol in the co-oxidation following its transition from the zero order to the first order with respect to the inhibitor, when in the absence of non-stationary branching of the reaction chains, a quasi-steady-state concentration of peroxy radicals is retained.

When the process obeys a zero-order kinetics, the rate of consumption of the inhibitor is constant

$$-\frac{dc_{\text{i}}}{dt} = V_{\text{i}} = \frac{c_{\text{i}0}}{t_{\text{ind}, \text{i}}} = \text{const}.$$

Thus, the time required for its complete consumption (*i.e.* the period co-oxidation) is equal to

$$t_{\text{ind}, \text{i}} = \frac{c_{\text{i}0}}{V_{\text{i}}}.$$

If we add the time t_0 for the propagation of reaction after the inhibitor has been exhausted to the above value, we obtain the dependence of the induction period on the initial concentration of phenol

$$t_{\text{ind}} = t_0 + t_{\text{ind}, \text{i}} = t_0 + \frac{c_{\text{i}0}}{V_{\text{i}}}.$$

The linear dependence $t_{\text{ind}}(c_{\text{i}0})$ holds over a wide range of monophenol concentrations.^{39–41} The length of the linear sections decreases appreciably in the presence of dialkyl sulfide. In this case, t_{ind} rapidly increases starting from a certain ‘critical’ $c_{\text{i}0, \text{cr}}$ value. A similar behaviour has also been observed in the presence of bisphenol 2246. In these systems, co-oxidation at $c_{\text{i}0} > c_{\text{i}0, \text{cr}}$ (and $c_{\text{ii}0} > c_{\text{ii}0, \text{cr}}$) obeys first-order kinetics and is characterised by an exponential equation

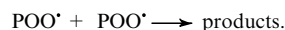
[†] In the presence of oxygen, the mechanism of hydroperoxide decomposition basically changes.

$$c_i = c_{i0} \exp(-k_i t)$$

or

$$\ln \frac{c_{i0}}{c_i} = k_i t.$$

This equation is valid until the $c_{i0,cr}$ value is attained. After that, the law for the termination of reaction chains changes, and their bimolecular termination in the subsequent steps begins:



In this case, the total induction period is characterised by the sum

$$t_{ind} = t_0 + \frac{1}{k_i} \ln \frac{c_{i0}}{c_{i,cr}}.$$

This relation holds fairly frequently.¹⁴

The above structural-kinetic model for the co-oxidation of the phenol and a polymer makes it possible to elucidate more precisely the physical meaning of the antagonistic influence of monophenol and bisphenol 2246 simultaneously introduced in a polymer.^{14, 39, 40} Although in this case, the overall content of inhibitors is larger, the induction period in the presence of these mixtures is shorter than that observed with bisphenol 2246 alone. The authors cited explained this phenomenon by a specific influence of monophenol and bisphenol on the emergence of radicals from the 'cage' of the hydroperoxide, which decomposes spontaneously. They believed that the monophenol destroys one of the radicals in a primary radical pair but prevents the destruction of the second radical; thus, the overall yield of radicals should increase. However, in the presence of bis-phenol 2246, which contains two functional groups, the yield of radicals increases to a lesser extent than in the presence of a monophenol or does not increase at all.

However, in contrast to these views, the data presented in Sections V and VI indicate that a typical monophenol, ionol, does not lead to any substantial increase in the yield of radicals from hydroperoxide. The kinetic model considered above makes it possible to give a simple explanation to the antagonistic effect.

Monophenol increases the rate of generation of co-oxidation v-chains by accelerating the injection of free valence from s-zones to v-zones of the polymeric-chain sponge. In this case, the term 'reaction cage' refers to a system of supermicropores in the structural s-zones rather than to a homogeneous environment consisting of macromolecular segments and resembling a structureless liquid.

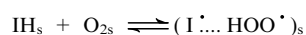
Monophenol reacts with the mediator peroxy radical and is thus converted into a quinoid alkoxy



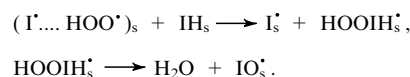
which cannot isomerise into the inactive phenoxyl. In this case, $\delta_i = k_m$, whereas in the reaction involving bisphenol 2246, $\delta_{ii} < k_m$ [Eqn (34)].

The competition between monophenol and bis-phenol for the s,v-transfer of radicals results in an increase in the rate of generation of the co-oxidation chains in v-zones of the polymeric matrix and thus shortens the induction period.

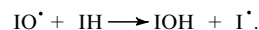
In conclusion, note that in the presence of sterically hindered monophenols considered in previous studies,^{41, 43} no transition to the first-order kinetics was observed over the whole range of monophenol concentrations studied. However, it cannot be ruled out that this transition would be possible in the presence of phenols in which the steric hindrance from the alkyl substituents is weaker or at a sufficiently high concentration c_i . For example, this situation can arise if the reversible dissociation of a complex of phenol with oxygen



competes with the following reaction



Diminution of steric hindrance can also be favourable for the appearance of an additional pathway to the termination of co-oxidation chains.



The reasons considered above might also account for the known fact that 4,4'-methylenebis(2-methyl-6-*tert*-butylphenol), which contains spatially separated OH groups in the molecule and is considered¹⁴ to be a weak antioxidant, is actually as effective as bisphenol 2246.⁴⁶ The termination steps mentioned above can also be among the reasons for the synergistic effect exhibited by antioxidant mixtures.

IX. Conclusion

A certain relationship between the microheterogeneous structure of the non-crystalline polymeric matrix and chemical transformations in the polymers has been mentioned in the literature long ago; this has been reflected in the polychromatic⁴⁷ (or polychromic)⁴⁸ kinetic model. However, individual studies in which this relationship was only stated, have not yet been united in a separate branch of the chemical physics of polymers. Description of kinetic polychromatism has reduced only to one or another variant of the formal mathematical scheme based on general physical views, without disclosing the in-depth causes for its origin.

It is clear that construction of adequate chemico-physical models for polymeric transformations requires inevitably that the supermolecular organisation of the polymeric reaction medium be known in detail. The microheterogeneous chain-sponge structure of polymer chains increases substantially the number of factors, which are able to influence in a particular way a chemical process involving them (compared to the number of factors influencing processes in a homogeneous liquid) and hampers the theoretical studies. Construction of structural kinetic reaction models¹⁰ is helpful in overcoming the arising difficulties (which is especially significant in the initial stage of the development of the theory).

The models for chain processes presented in this review have been constructed with allowance for the fine structure of polymer chain-sponge micelles, which contain a sponge framework possessing a certain degree of mobility. In these models, the notion of mobility is associated with the property of micropores to change their sizes under the influence of thermofluctuational motion of cooperated units of flexible polymer chains within the microporous sponge structure rather than with the abstract concept of 'molecular segmental mobility'.

The method of structural-kinetic modelling made it possible to discover important regimes of chain reactions, such as heterogeneous-heterophase and heterogeneous-homophase regimes, and to refine the concept of 'latent radical' (intracage) processes occurring inside a thermofluctuationally excited micropore, which has expanded to the size of a supermicropore.

The construction and analysis of various reaction models proved the validity of the general concept of the chemistry of the microheterogeneous polymeric-chain sponge. This concept provides extensive possibilities for further specification of the mechanism of elementary chemical steps occurring in a fluctuating sponge material. In addition, it requires that researchers change their attitude to some generally accepted views concerning the homogeneous character of non-crystalline polymers (in terms of the homogeneous model, a kinetically unstable unit, which is formed and destroyed by fluctuations, has a 'short-range' order in the arrangement of segments, and resembles the areas with a short-range order in liquids, is considered as the only structural element).⁴⁹

In particular, the interpretation of the self-acceleration stage in the oxidation of polyalkenes within the framework of the non-stationary branched chain mechanism should be rejected.

It is also believed¹⁴ that the absence of substantial deviations from the first-order kinetics indicates that the inhibitor is mostly consumed in its direct interaction with oxygen and in the steps of termination of the oxidation chains thus generated. However, in reality, as shown in our review, the greater part of phenol is consumed *via* its chain co-oxidation with the polymer, no matter what particular order — zero or first — with respect to the inhibitor is obeyed by the process.

The criterion used in the inhibitor method for determination of the rate of generation of oxidation chains in homogeneous liquids¹⁵ also loses its fundamental significance when applied to polymers. The zero order for consumption of an inhibitor in a microheterogeneous chain-sponge medium does not imply any longer, as it does in a homogeneous liquid, that the inhibitor is not involved in any step other than termination of reaction chains. The inhibitor molecules, which occur in a polymeric matrix and scavenge all the reaction chains, can liberate fairly reactive radicals, together with inactive ones. Thus, the inhibitor becomes an active participant in the co-oxidation with the polymer.

The structured character of the chain-sponge polymeric matrix also causes the need to determine separately the non-equivalent rates of radical generation, firstly, in quasi-steady-state zones consisting of relatively immobile supermicropores, secondly, in dynamically more active zones in which the oxidation chains of macromolecules propagate, and, thirdly, at the stage of the interzone transfer of radicals. Simultaneously, this gives rise to the problem of development of experimental methods for determining the rate constants for the elementary reactions, which characterise heterogeneous steps in the polymeric-chain sponge.

This review is a logical continuation of the studies performed by Academician N M Emmanuel and his school dealing with oxidation processes in the condensed phase.^{50–54}

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^d — *Russ. Polym. Sci. (Engl. Transl.)*

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Unusual transformations of 2-isoxazolines

E V Koroleva, F A Lakhvich

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Abstract. The data on unusual transformations of 2-isoxazolines observed in both their preparation by traditional methods and various reactions, mostly with nucleophilic reagents, are considered systematically. Possible mechanisms of these reactions are discussed. Special attention is given to the transformations of 2-isoxazolines under the action of complex organometallic compounds. The bibliography includes 78 references.

I. Introduction

Isoxazoles and their dihydro derivatives, 2-isoxazolines (hereinafter, isoxazolines), are synthetic precursors of various acyclic compounds. They are widely used in organic synthesis for obtaining β -hydroxy ketones and β -diketones, γ -amino alcohols, enoximes, enones, and β -amino enones. Owing to the versatility of the nitrile oxide method of preparing isoxazoles and isoxazolines and the latent bifunctionality of the isoxazole heterocycle, the so-called 'isoxazoline pathway'¹ developed in the last two decades has become a recognized procedure for the total synthesis of natural compounds, including antibiotics, nucleosides, alkaloids, vitamins, steroids, and prostanoids.

The use of isoxazoles in a total chemical synthesis of natural compounds and the related aspects of the preparation and transformations of isoxazoles and isoxazolines have been surveyed in a number of reviews.^{1–5}

The main attention in these reviews has been concentrated on the reductive cleavage of the heterocycle at the N–O bond. This reaction is a traditional method of realisation of the latent bifunctionality of the isoxazole ring. At the same time, after the discovery of selective reductive cleavage of the heterocycle, the reactions of isoxazolines with nucleophilic reagents, which had been earlier the subject of intense studies of the properties and transformations of the isoxazole ring, failed to attract further attention of investigators, since they did not find wide synthetic application, except for the cleavage of 3-non-substituted isoxazolines into hydroxy nitriles⁶ and of 3-substituted isoxazolines into enoximes.⁷

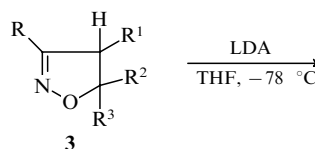
However, recently considerable attention has again been expressed in the transformations of isoxazolines under the action of nucleophilic reagents. The reason for this is, first and foremost, the application in modern organic synthesis (including the isoxazoline chemistry) of new reagents, in particular complex organometallic systems. The use of organometallic reagents, in which the reductive capacity is combined with their properties as bases, has led to the discovery of transformations, which are unusual for isoxazoline compounds. Information about the state-of-the-art of these unusual reactions of isoxazolines is systematised and considered in the present review.

II. Interaction of 2-isoxazolines with bases

The molecule of 2-isoxazoline (**1**) having two heteroatoms with lone electron pairs and an unsaturated C=N bond is characterised by an uneven distribution of the electron density over the ring and by the presence of potentially mobile ('acidic') hydrogen atoms at C(3), C(4), and C(5). Under the action of a base, deprotonation can occur, which is accompanied by the generation of one of the possible cyclic carbanions (**2a–e**) (Scheme 1).

3- or 4-Non-substituted isoxazoline derivatives undergo cleavage under the action of bases. It is the protons at these carbon atoms that are the most 'acidic' as regards the distribution of electron density in the isoxazoline molecule. Thus, the interaction of C(3)-non-substituted isoxazolines with bases gives the isoxazolinium anion **2a**. Upon subsequent cleavage of the N–O bond, the isoxazoline derivative is transformed into a compound with a hydroxynitrile group.^{6, 8–10}

The 3-substituted 2-isoxazolines **3** are cleaved only in the presence of strong bases. This reaction has been extensively and systematically studied by Jager et al.^{2, 7, 11–13} In the first step, a strong base abstracts the proton from the C(4) atom (4-*endo*-deprotonation) with the formation of an isoxazolinium anion of the type **2b** (Scheme 1), which is stable at $-60\text{ }^{\circ}\text{C}$ to $-80\text{ }^{\circ}\text{C}$ and cleaves at room temperature to give a non-cyclic enoximate anion and then the enoxime **4**.

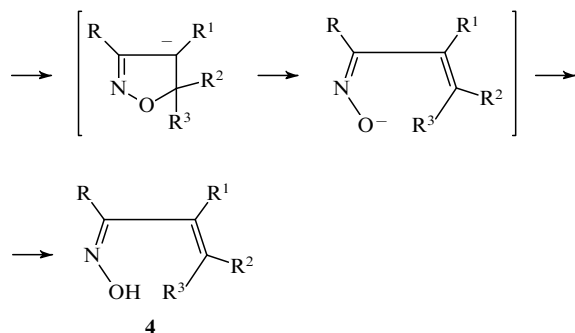
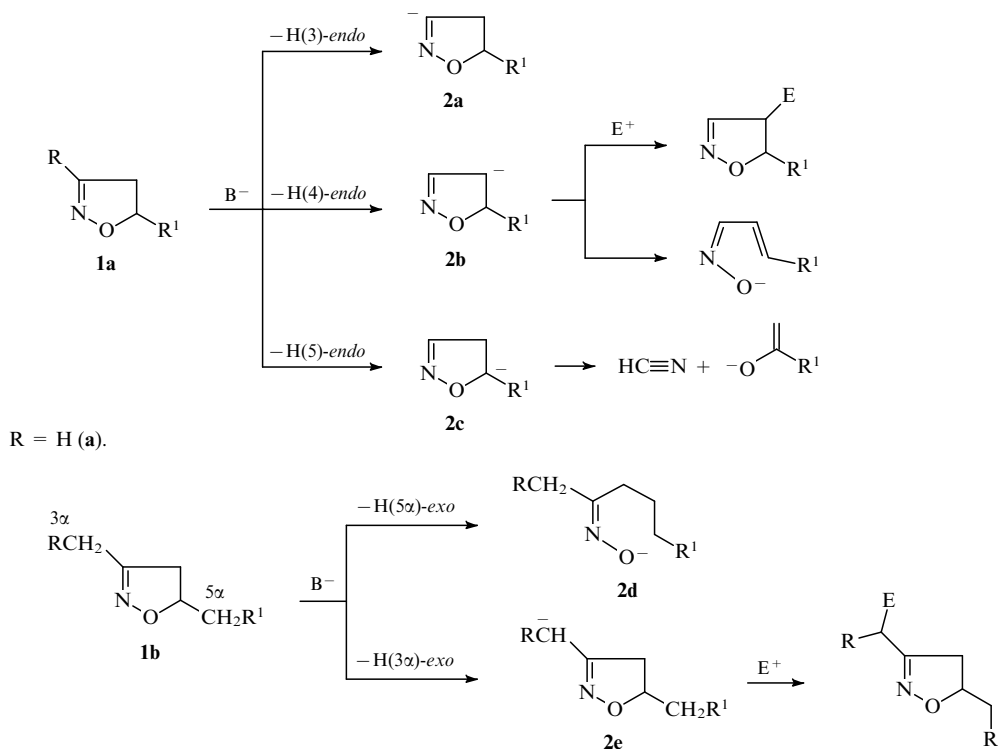


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Scheme 1



Various preparative methods have been developed for the cleavage of isoxazolines into unsaturated oximes with lithium diisopropylamide (LDA)^{7, 14} and dimethylsodium.¹⁵ These methods have found wide application in the synthesis of polyfunctional organic (including natural) compounds.^{3, 16–18}

If the isoxazoline contains alkyl substituents, 4-*endo*-deprotonation competes with *exo*-deprotonation; however, it has been established that the 4-*endo* proton possesses a higher acidity and is the first to be deprotonated under standard conditions for this reaction (–78 °C, LDA).¹⁸ With respect to the ease of abstraction by bases, the hydrogen atoms of *C*-alkyl-2-isoxazolines can be arranged in the following order: 3-*endo* > 4-*endo* > 3-*exo* > 5-*endo*.

Jager¹² has proposed a generalised scheme, which includes four possible pathways of transformations of the 3-substituted isoxazoline heterocycle under the action of bases (see Scheme 1). The mobility of the H(4) protons of the isoxazoline ring can be employed for the introduction of substituents into the isoxazoline molecule using the so-called ‘Jager alkylation’ method.^{7, 11–13, 17–19} Alkylation of the anions **2b** and **2e** by electrophiles is used for the modification of the heterocycle and subsequent generation of a functionalised acyclic compound from the isoxazoline derivative.^{2, 3}

Analysis of a great number of publications has revealed that an unambiguous result can hardly be achieved in reactions with bases due to a number of factors intervening. The main factors are the structure of the substrate and the nature of the base interacting

with it. The direction and ease of the isoxazoline ring cleavage depend on the particular structure of the isoxazoline derivative, in the first place, on the distribution of electron density in the molecule.^{20, 21} The presence or the absence of substituents at the carbon atoms of the heterocycle and their electronic effect on the ring eventually determines the site of deprotonation under the action of the base. Clearly substituents having polarised bonds, heteroatoms, etc., can influence critically the direction of the reaction. Such situations will be the subject of our further consideration.

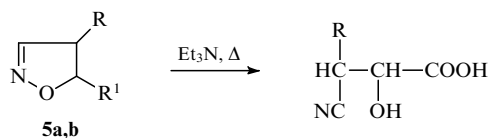
III. 1,4-Cycloreversion of 2-isoxazolines

Cycloreversion of isoxazolines (degradation of the heterocycle at two bonds) often interferes with normal (usual) isoxazoline ring cleavage under the action of basic (as well as organometallic and some other) reagents normally occurring at one of the bonds of the N–O–C fragment. Two types of ring fission (in accord with the number of C–C bonds present in the heterocycle) are known for isoxazolines, *viz.*, 1,3- and 1,4-scission.

Ring fission always occurs with rupture of the bond between the heteroatoms, since this bond is the weakest in the ring. Most probably, it is the C=N–O fragment of the ring, that interacts with the reagent. For example, it has been noted that chelation of various reducing reagents (e.g., complex metal hydrides, hydrogenation catalysts, etc.) in reductive cleavage reactions occurs with the involvement of this particular fragment of the isoxazoline molecule.¹⁸ The site of the second ring fission is one of the two C–C bonds, namely: C(3)–C(4) in the case of 1,3-cycloreversion and C(4)–C(5) in the case of 1,4-cycloreversion. In the reaction with a nucleophile (with a base), the reaction center is the carbon atom carrying the most acidic proton. The site of the second fission of the ring is largely determined by the specific structure of the isoxazoline molecule, e.g., by the presence of substituents, which can affect the distribution of electron density at the ring atoms.

Thus, cycloreversion, which normally accompanies the main (usual) direction of the reaction, poses the problem of practical synthesis of hydroxynitriles from isoxazolines. The highly stereoselective reaction of isoxazoline cleavage into hydroxynitriles was

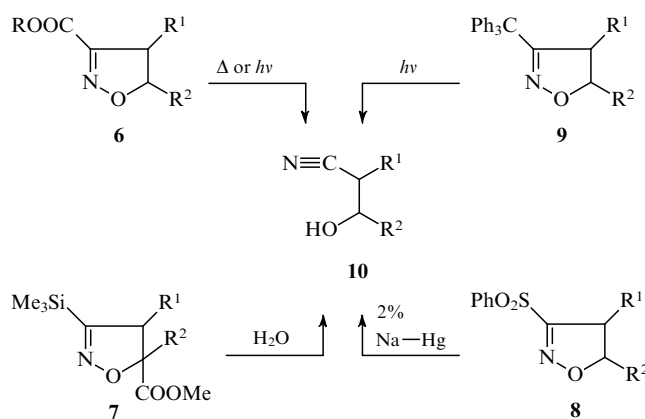
first described by Huisgen et al.⁶ for isoxazoline-5-carboxylic acid (**5a**) and 4-methylisoxazoline-5-carboxylic acid (**5b**), which produced quantitatively 3-cyano-2-hydroxypropionic and 3-cyano-2-hydroxybutyric acids upon treatment with triethylamine.⁶



R = H (**a**), CH₃ (**b**); R' = COOH.

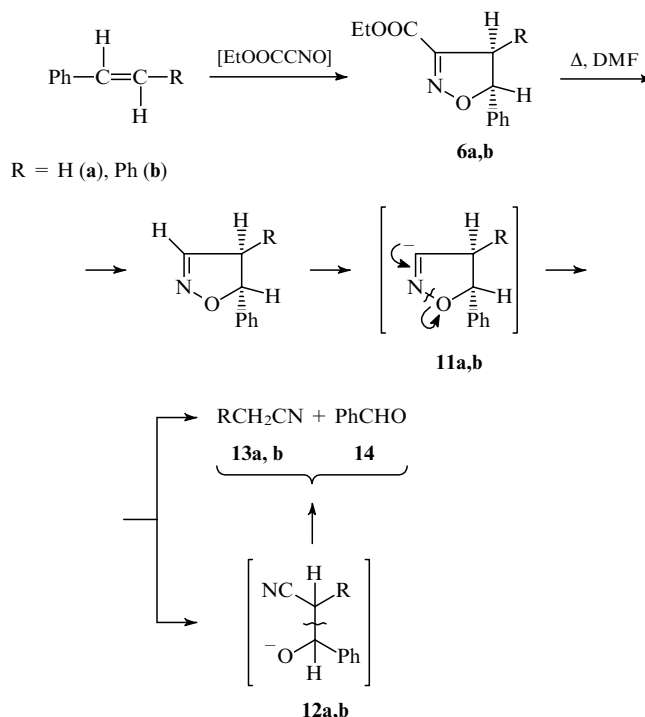
Cleavage of other 3-non-substituted isoxazolines under the action of bases occurred in a similar way.^{22,23} Consecutive 1,3-dipolar cycloaddition of nitrile oxides to alkenes and basic cleavage of 2-isoxazolines thus formed is a rather simple, versatile and stereospecific method for preparing vicinal hydroxy nitriles.

The scope of this method has been expanded with the use of 3-substituted 2-isoxazolines **6–9**, which could generate under certain conditions either the 3-non-substituted isoxazolines **5** or the corresponding anion or radical. Thus, the photolytic or pyrolytic decarboxylation of isoxazoline-3-carboxylic acids and their derivatives **6** was accompanied by simultaneous cleavage of the heterocycle to give the β-hydroxynitriles **10**.^{24–26} 3-Triphenylmethyl-2-isoxazolines **9**,²⁷ 3-trialkylsilyl-2-isoxazolines **7**,²⁸ and 3-phenylsulfonyl isoxazolines **8**^{22,25} underwent similar cleavage. These methods turned out to be useful in the solution of a number of synthetic problems and are now widely used in the synthesis of polyfunctional compounds.^{6, 10, 25, 28–33} Compounds **5–9** behave similarly in the above reactions and, as will be shown below, the mechanisms of cleavage (cyclodegradation) of the isoxazoline heterocycle are identical. Therefore, all these reactions including the interaction with nucleophilic reagents, as well as pyrolytic and photolytic degradation, are considered in the same section.



Pyrolytic decarboxylation of isoxazoline-3-carboxylic acid derivatives devoid of aromatic substituents gives the β-hydroxynitrile **10** in a quantitative yield. However, in many cases other products form in addition to the hydroxynitriles **10**. Heating of ethyl 5-phenylisoxazoline-3-carboxylate **6a** at 120–130 °C results in the hydroxynitrile **10** (R¹ = H, R² = Ph) (65%–90%) and trace amounts of benzaldehyde. Ethyl isoxazoline-3-carboxylate **6b** (R = Ph) prepared from *trans*-stilbene gives quantitatively under identical conditions a 1 : 1 mixture of phenylacetaldehyde (**13**) and benzaldehyde (**14**), the products of cyclodegradation at the N–O bonds (the anion **11b**) and C(4)–C(5) (the alkoxide ion **12b**) (Scheme 2).²⁶

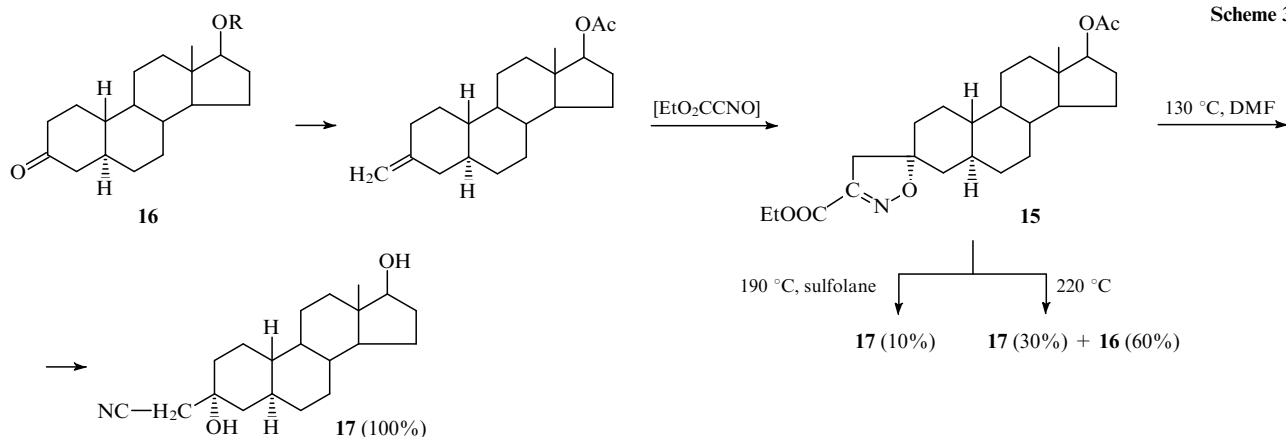
Scheme 2

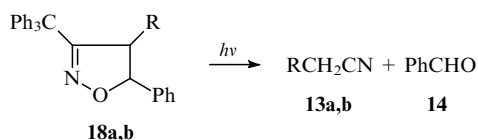


The steroid isoxazoline **15** obtained from the ketone **16** gives quantitatively the hydroxynitrile **17** (1 h, 130 °C, DMF). However, at 220 °C the yield of the hydroxynitrile **17** is 30% and the yield of the ketone **16** is 60%, while in sulfolane (190 °C, 30 min) the yield of the hydroxy nitrile is as low as 10% (Scheme 3).²⁶

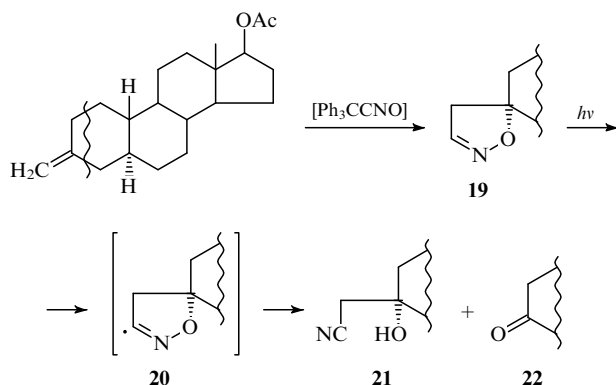
Upon photolysis, 5-phenyl-3-triphenylmethylisoxazoline (**18a**) and 4,5-diphenyl-3-triphenylmethylisoxazoline (**18b**) prepared from styrene and *trans*-stilbene, respectively, gave different amounts of benzaldehyde. Under these conditions, the steroid isoxazoline **19** was converted (via the radical **20**) into a mixture of the ketone **22** (up to 48%) and the hydroxy nitrile **21** (up to 5%).²⁷

Scheme 3



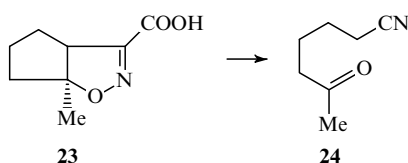


R = H (**a**); R = Ph (**b**).



The mechanism of cyclodegradation proposed by Kaufmann and Kalvoda^{26,27} involves generation of a cyclic carbanion **11**. Subsequent cleavage of the weakest N–O bond gives either the acyclic alkoxide ion **12** or the nitrile **13** and the aldehyde **14** as a result of synchronous heterocycle fragmentation, depending on the strength of the C(4)–C(5) bond. Thus, the cyclodegradation of the carbanion **11** may occur either consecutively: **11** → **12** → **13** + **14**, or synchronously: **11** → **13** + **14** (see Scheme 2). Apparently, the degradation of the photolytically generated radical **20** occurs by an analogous scheme.

The result of conversion of the 3-phenylsulfonylisoxazolines **8a–h** depends on the structure of the substituents at the C(4) and C(5) atoms of the heterocycle (Table 1). Thus, the reaction of phenylsulfonyl derivatives **8a–f** with sodium amalgam gives 86%–94% of the corresponding hydroxy nitriles as the sole diastereomers. It is worthwhile noting that the 3-phenylsulfonyl derivative **8f** is cleaved into the corresponding hydroxy nitrile (**10f**), while the isoxazoline-3-carboxylic acid (**23**) gives upon decarboxylation only 6-oxoheptanonitrile (**24**), the product of the cyclodegradation at the C(4)–C(5) bond:²⁵



Upon treatment with sodium amalgam, 3-phenylsulfonyl-4,5-diphenylisoxazolines **8g,h** give the same cyclodegradation products, **13b** and **14**^{22,23} as those formed upon decarboxylation of 4,5-diphenylisoxazoline-3-carboxylic acid.²⁶ The composition of the base-induced cleavage products also depends on the pH of the reaction medium: in a phosphate buffer, a mixture of hydroxy nitrile, benzyl alcohol (the product of subsequent reduction of benzaldehyde with sodium amalgam), and phenylacetaldehyde is formed. It has been noted that at pH > 10 the cyclodegradation products form predominantly, whereas at pH < 9 hydroxynitriles form (in this case, the conversion is insignificant). Since in an aqueous sodium hydroxide solution the conversion of the hydroxy nitriles prepared from the isoxazolines **8g,h** into benzaldehyde and phenylacetaldehyde was completed within several minutes, it may be supposed that the latter are the products of the retroaldol reaction of the hydroxy nitrile, since the latter is alkali-labile. However, it is very likely that both the N–O cleavage of the isoxazoline ring into the hydroxy nitrile and the competing process of cyclodegradation occur by the same mechanism, in

which the cyclodegradation is one of the pathways of stabilisation of the cyclic carbanion **11** or the acyclic alkoxide ion **12**.

The anion **11**, which has been postulated for the cyclodegradation of the isoxazoline-3-carboxylic acids **6**,^{26,27} seems to be the intermediate product in the cleavage of 3-non-substituted (**5**),⁶ 3-phenylsulfonyl- (**8**),²² and 3-trimethylsilylisoxazolines (**7**),²⁸ although direct evidence in favour of this mechanism has not been obtained yet. The generation of the isoxazolinium anion **11** from 3-phenylsulfonyl-, 3-trimethylsilyl-, and 3-carboxyisoxazolines occurs by the cleavage of the C(3)–X (X = S, Si, C) bond. It is worth noting that the identity of the products of the above reaction points to the common intermediate, which can be represented by the corresponding 3-non-substituted isoxazoline generating the anion (or the radical). If the C(4)–C(5) bond cleavage occurs and the β-hydroxy nitrile is thermally stable under the given reactions conditions, one may postulate the cyclodegradation as occurring via the intermediate formation of the acyclic alkoxide ion **12**.²⁶ An alternative mechanism of this reaction is the concerted cyclodegradation of the carbanion **11** with the formation of compounds **13** and **14**.²⁵

The cleavage of the alkoxide ion **12** must be very rapid and compete with protonation. Thus, the observed conversion of the β-hydroxy nitrile **10f** into the oxonitrile **24** under the action of a

Table 1. Cleavage of 3-benzenesulfonylisoxazolines **8a–h** by sodium amalgam into hydroxy nitriles **10a–h**.²¹

3-Benzenesulfonylisoxazolines (8)	β-Hydroxy nitriles (10)	Yield (%)
		91
		94
		89
		86
		83
		93
		0
		0

base (170 °C) is in accord with the rapid cleavage of the C(4)–C(5) bond in the alkoxide ion.²² Presumably, in the course of decarboxylation the alkoxide anion **12** is originally generated in an excited state; such a 'hot' alkoxide ion undergoes fragmentation more easily.

If isoxazolines are considered as a latent form of β -hydroxy ketones and the process of the formation of isoxazolines and their cleavage into hydroxy ketones as the equivalent of the aldol condensation, the 1,4-cycloreversion represents, in effect, a retroaldol degradation.

Apart from the above examples of 1,4-cyclodegradation of the isoxazoline ring, when the generation of the isoxazolinium anion of type **2a** proceeds with the participation of nucleophilic reagents, an alternative way of 1,4-cycloreversion of isoxazolines is known, which represents the degradation of the isoxazoline ring without deprotonation and is accompanied by the formation of two carbonyl compounds. Such a cyclodegradation was observed as a competing process in the cleavage of isoxazolines by metal polycarbonyls.^{34–38}

In 1984–1987, preparative methods were developed for thermolytic and photolytic degradation of isoxazolines into β -hydroxy ketones in the presence of metal polycarbonyls.^{34, 35, 37} This interaction is not unambiguous, however. Thus, in the case of phenyl-substituted isoxazolines **25a,b**, the aldehydes **26** and the ketones **27** form, which are the products of retroaldol degradation of the heterocycle at the N–O and C(4)–C(5) bonds (Scheme 4). The isoxazolines containing no substituents at C(5) give, in addition to the 1,4-cycloreversion products, the corresponding β -hydroxyketones **28** or aminoenones. It was also found that 1,4-cycloreversion is the main pathway of the cleavage of isoxazolines with $\text{Mo}(\text{CO})_6$ in anhydrous media.³⁷

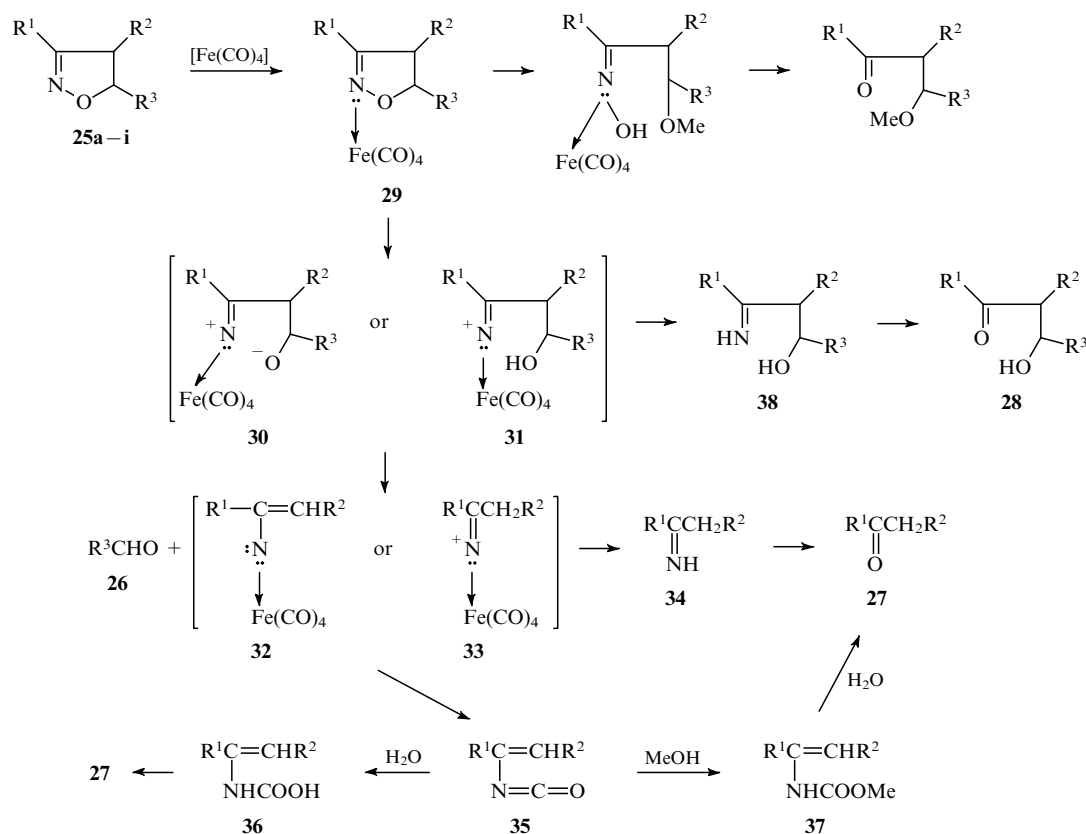
The yields of the products of photolytic [under the action of $\text{Fe}(\text{CO})_5$] and thermal [under the action of $\text{Fe}_2(\text{CO})_9$] cleavage of the isoxazolines **25a–i** are listed in Table 2.³⁴ The results presented can be explained within the framework of the mechanism of cyclodegradation depicted in Scheme 4. The most probable mechanism is the degradation via the intermediate **29** and its cleavage with the formation of a bipolar complex **30**, the rapid hydrolysis of

Table 2. Photolytic cleavage of 2-isoxazolines by iron polycarbonyls during photolysis.³⁴

Compounds	R ¹	R ²	R ³	Time /h	Yield (%)		
					26	27	28
25							
a	Ph	H	Ph	24	57	69	–
a^a	Ph	H	Ph	6	73	81	–
b	Ph	Ph	Ph	10	62	96	–
b^a	Ph	Ph	Ph	3	42	84	–
c	Ph	H	Hexyl	24	52	86	–
c^a	Ph	H	Hexyl	4	–	53	30
d	Me	H	Ph	2	53 ^b	57 ^b	–
e	Me	H	Hexyl	6	61 ^b	54 ^b	–
f	Ph	H	Vinyl	24	54 ^b	78 ^b	–
g	Mesyl	H	Ph	6	6	58	91
h	Ph	H	H	19	see ^c	35	60
i	Ph	Me	H	5	see ^c	45	40

^a Thermal treatment; ^b isolated as 2,4-dinitrophenylhydrazone; ^c not isolated.

which gives the β -hydroxy ketone **28**. In anhydrous media, the cleavage occurs at the C(4)–C(5) bond. An n -donor complex **29** of isoxazoline with $\text{Fe}(\text{CO})_4$ generated photochemically from $\text{Fe}(\text{CO})_5$ or thermally from $\text{Fe}_2(\text{CO})_9$ cleaves to give the intermediates **30** or **31**, which undergo further degradation to yield the aldehyde **26** and the vinylidene complex **32** (or its protonated form **33**). Obviously, the factor facilitating the easy cleavage of the N–O bond is the delocalisation of the π - d electrons from Fe to the π^* -orbital of the C=N–O fragment of the heterocycle. In methanol (or in the presence of water), the complex **32** undergoes reduction to give the imine **34** (major pathway) or insertion of the carbonyl occurs with the formation of the vinyl isocyanate **35** (minor pathway). The isolation of a stable methyl mesyl ketimine in the case of the isoxazoline **25g** is evidence for the intermediate formation of the corresponding imine **34**. In the presence of water,



the vinyl isocyanate **35a** ($R^1 = \text{Ph}$) dissociates into the ketone **27a** via the intermediate acid **36**, and in methanol it gives 1-phenyl-vinylcarbamate **37a**. The imine **34a** is hydrolysed when treated with water (or in the presence of water) to give the ketone **27a**. Thus, the intermediates **32** (or **33**) are very labile in protic media or in the presence of trace amounts of water. The carbamate **37** can also undergo hydrolysis into the ketone **27**. The formation of the latter can also occur through consecutive transformations of the intermediates **32** (or **33**) into the imine **34**.³⁴

The nature of the substituent at the C(3) atom does not apparently influence appreciably the course of the reaction. Thus, for 3-methyl- (**25e**) and 3-phenyl-substituted (**25a**) isoxazolines the results of the reaction are comparable (Table 2). Obviously, the substitution at C(5) is the most important for the cleavage of the C(4)–C(5) bond. The absence of substituents at C(5) prevents this cleavage. Thus, for the C(5)- non-substituted 2-isoxasolines **25h,i**, the yield of the aldol degradation products, *viz.*, acetophenone **27h** and propiophenone **27i**, was about 40%, whereas the corresponding hydroxyketones **28h,i** were obtained with the yields of about 50%. Apparently, in these cases the energy barrier for the C(4)–C(5) bond cleavage is higher than that for the 3-substituted isoxazolines **25a–g**, and the degradation of the **30** (**31**) $\rightarrow$ **26** + **32** (**33**), type involving the elimination of the aldehyde molecule, competes with the cleavage via the hydroxy imine **38** into the hydroxyketone **28**. Irradiation of the isoxazolines **25h,i** with $\text{Fe}(\text{CO})_5$ in methanol does not cause the aldol-type reversion.

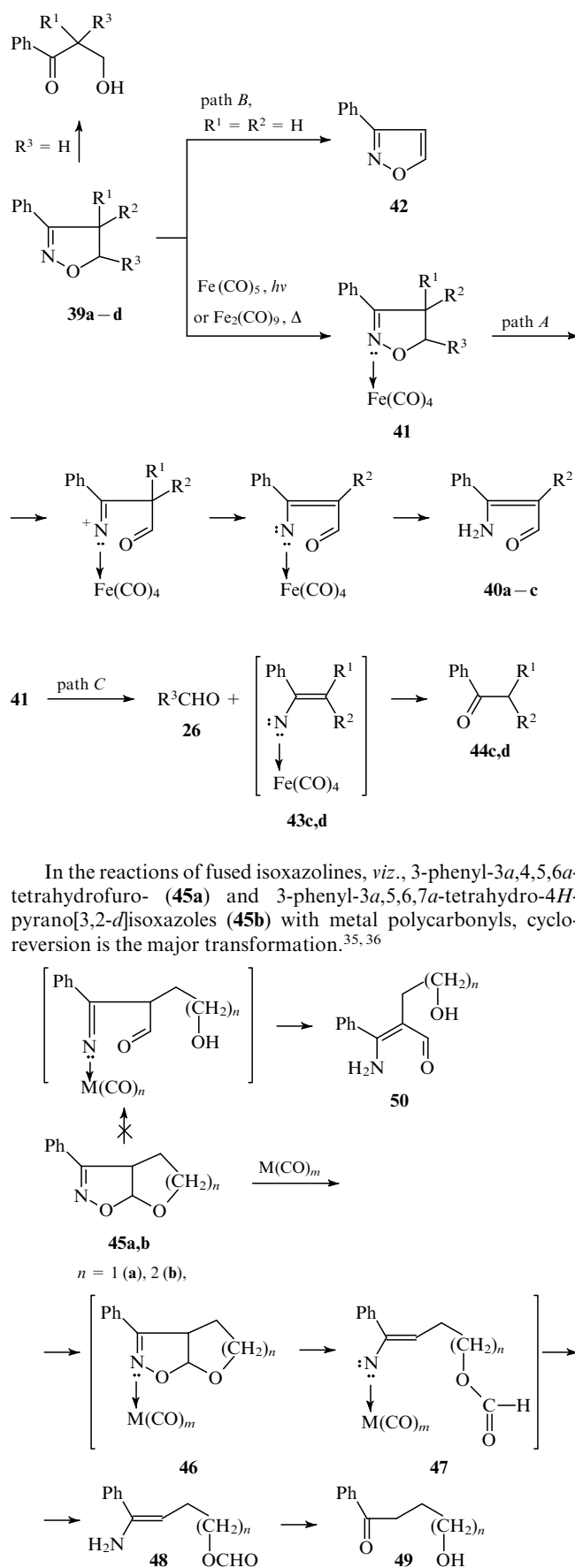
Reactions of isoxazolines **39a–c** having acetoxy, ethoxy, or amino groups at C(5) with metal polycarbonyls give β -amino enones **40a–c** in good yields under identical conditions (Table 3).^{34,36} The enamino ketone **40** can form from the complex **41** by cleavage at the N–O bond and subsequent elimination of the AcO- or EtO-groups to give the vinylnitrene complex (pathway *A*, Scheme 5) similar to the complex **31**. An alternative pathway for obtaining the enamino ketones **40**³³ (pathway *B*, Scheme 5), through elimination of AcOH and EtOH from isoxazolines with the intermediate formation of the corresponding isoxazoles **42** and their degradation by metal polycarbonyls has been described.³⁹ This pathway seems to be analogous to aromatisation of isoxazolines, which will be considered below. The pathway *C* depicted in Scheme 5 is analogous to the degradation of isoxazolines **25a–g** and involves the elimination of the aldehyde **26** with the formation of the vinylnitrene complex **43**, which is further converted into the ketone **44**. In the case of isoxazoline **39c** having a pyrrolidino substituent at C(5), the products of conversion by both the pathway *A* and the pathway *C* have been isolated. The direction of this reaction is also affected by the substituents at C(4) of the heterocycle. For 4,4-dimethyl-5-(pyrrolidino-2-isoxazoline (**39d**), only one pathway *C* resulting in the formation of the ketone **44d** is realised, since for $R^1 \neq \text{H}$, the elimination of the tertiary amine molecule is unlikely.

Scheme 5

Table 3. Photolytic cleavage of the 2-isoxazolines **39a–d** by iron polycarbonyls during photolysis.³⁴

Com- pounds 39	R^1	R^2	R^3	Time /h	Yield (%)	
					44	40
a	H	H	OAc	6	80	0
a^a	H	H	OAc	3	79	0
b	H	H	OEt	24	76	0
c	H	Et	$-\text{N}(-\text{CH}_2-)_4$	24	35	51
d	Me	Me	$-\text{N}(-\text{CH}_2-)_4$	20	0	72

^a Thermal treatment.



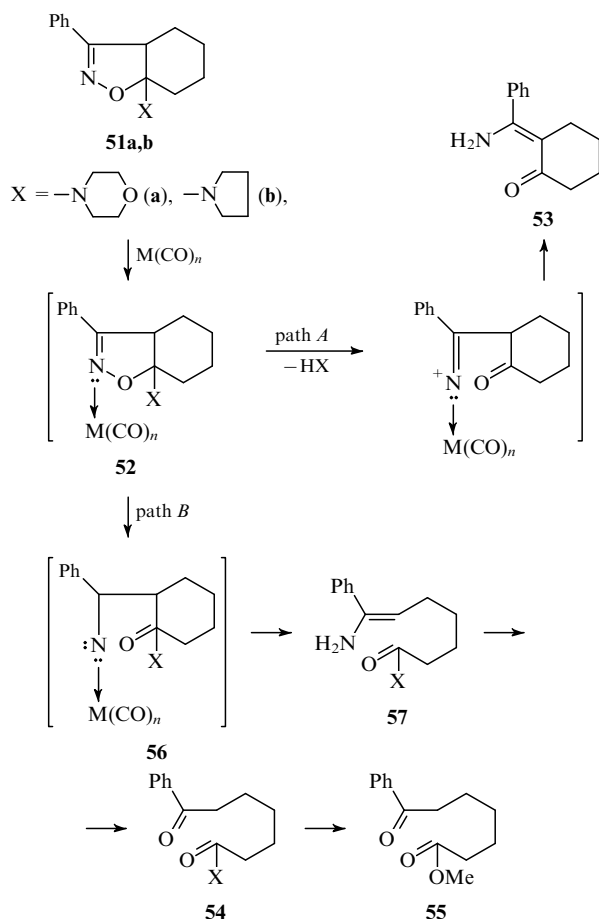
In the reactions of fused isoxazolines, *viz.*, 3-phenyl-3a,4,5,6a-tetrahydrofuro- (**45a**) and 3-phenyl-3a,5,6,7a-tetrahydro-4H-pyrano[3,2-*d*]isoxazoles (**45b**) with metal polycarbonyls, cycloreversion is the major transformation.^{35,36}

$\text{M}(\text{CO})_m = \text{Fe}(\text{CO})_4, \text{Mo}(\text{CO})_6; [\text{Fe}_2(\text{CO})_9, \Delta \rightarrow \text{Fe}(\text{CO})_4; \text{Fe}(\text{CO})_5, \Delta \rightarrow \text{Fe}(\text{CO})_4]$.

The degradation proceeds via the n -donor complex **46**, which is cleaved to give a nitrene complex **47**; its further reduction results in the enamine **48**, which is hydrolysed under the reaction conditions into the hydroxyketone **49**. An alternative pathway with the formation of the enamino ketone **50** resulting from the cleavage of the N—O bond of the isoxazoline and the C—O bond of pyran does not take place, in contrast to the cleavage of 5-ethoxy- or 5-acetoxyisoxazolines.

Similar reactions with 7*a*-morpholino- (**51a**) and 7*a*-pyrrolidino-3-phenyl-3*a*,4,5,6,7,7*a*-hexahydrobenzo[*d*]isoxazoles (**51b**) give the products **53** and/or **55**, depending on experimental conditions. With $\text{Fe}_2(\text{CO})_9$ (thermolysis) or $\text{Fe}(\text{CO})_5$ (photolysis), the degradation follows predominantly pathway *A* (Scheme 6) to give the enamino ketone **53** formed as a result of cleavage of the N—O bond and the elimination of the amine HX. Treatment of isoxazolines **51** with molybdenum hexacarbonyl in methanol gives, in addition to the products **53** and **55**, also a small amount of the oxo amide **54**. The degradation of the intermediate complex **52** at the N—O and C(3*a*)-C(7*a*) bonds can also occur via the intermediate **56**, the reduction of which and subsequent hydrolysis gives the enamino amide **57** (pathway *B*, Scheme 6). The derivative **55** is the product of methanolysis of the amido group in the compound **54**.³⁵

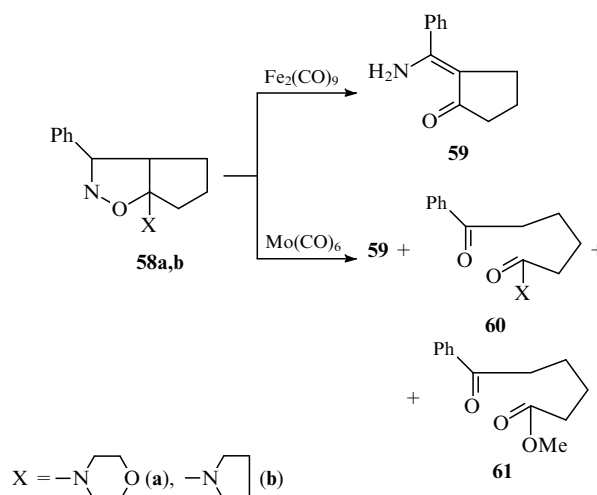
Scheme 6



$\text{M}(\text{CO})_n = \text{Mo}(\text{CO})_6, \text{Fe}(\text{CO})_4$.

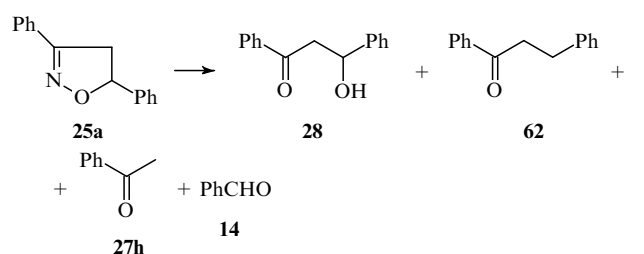
On the other hand, the reaction of 6*a*-morpholino- (**58a**) and 6*a*-pyrrolidino-3-phenyl-3*a*,5,6,6*a*-tetrahydro-4*H*-cyclopenta[*d*]isoxazolines **58b** with $\text{Fe}_2(\text{CO})_9$ is a very slow process, and the β -enamino ketones **59** are isolated along with large quantities of the original isoxazolines. At the same time, the enamino ketone **59**, the amide **60**, and the ester **61** are readily formed with $\text{Mo}(\text{CO})_6$.³⁵

In the above examples, a dependence emerged between the direction of isoxazoline degradation and the length of the



4,5-polymethylene chain. Presumably, the composition of the products does not depend on the structure of the leaving group X. However, the cleavage of the N—O bond with simultaneous elimination of the heterocyclic amine and the formation of the enamino ketones **59** becomes the major pathway for the fused isoxazolines **58**.

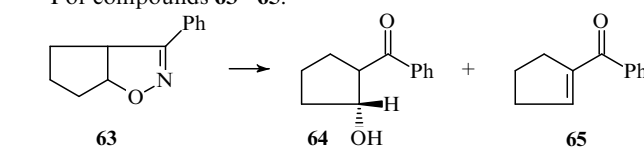
It should be noted that the cycloreversion, which interferes with the degradation of 3-phenyl-substituted isoxazolines, is not characteristic of 3-alkyl-substituted ones. In the latter case, the degradation of the heterocycle under the action of metal polycarbonyls follows a traditional pattern with the formation of the corresponding hydroxy ketones and enones. A modified procedure has been proposed to block the cycloreversion, which occurs in the reaction of the 3,5-diphenyl-substituted 2-isoxazolines **25** with metal polycarbonyls, in which the reagent is the $\text{Mo}(\text{CO})_3(\text{MeCN})_3$ complex.³⁸ In this case, the proportion of the cycloreversion products **14** and **27h** formed upon cleavage of the 3,5-diphenyl-2-isoxazoline **25a** diminishes from 40% down to 4%.



	Method	Recovery of the starting material (%)	Yield (%)			
			28	62	27h	14
25a	A ^a	27–30	21–39	16–27	2	2
	B ^b	—	16	20	25	13

^a A — $\text{Mo}(\text{CO})_3(\text{MeCN})_3$. ^b B — $\text{Mo}(\text{CO})_6$, MeCN, H_2O , 1.5 h.

For compounds **63–65**:

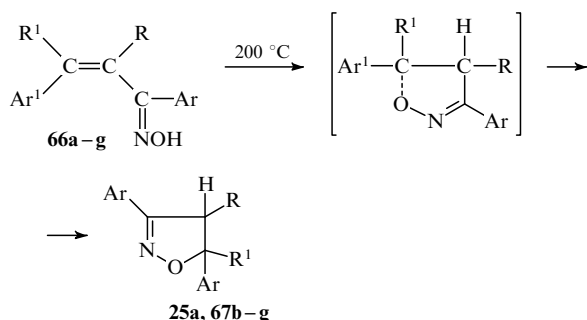


	Method	Recovery of the starting material (%)	Yield (%)	
			64 (cis : trans)	65
63	A	45–52	27–38 (1.5)	10–17
	B	32	24 (5)	10

IV. 1,3-Cycloreversion of 2-isoxazolines

If the 1,4-cycloreversion of 2-isoxazolines considered above represents a retroaldol degradation, the 1,3-cycloreversion is a process which is the opposite of intramolecular cycloaddition. The reaction of retro-1,3-dipolar intramolecular cycloaddition takes place primarily in the synthesis of isoxazolines from oximes.

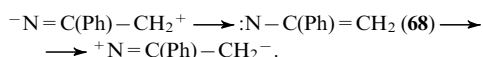
Thus, Shotton et al.⁴⁰ observed 1,3-cycloreversion of isoxazolines in the studies of thermal cyclisation of the oximes **66a–g**. At temperatures around 300 °C, oximes yield compounds, which can be regarded as products of fragmentation of the intermediate isoxazolines undergoing 1,3-cyclodegradation.⁴⁰ These isoxazolines were isolated if the cyclisation of the oximes **66a,b** was carried out at 200 °C, and then at 300 °C they decomposed into the same products as those obtained upon thermal cyclisation of oximes at 300 °C.



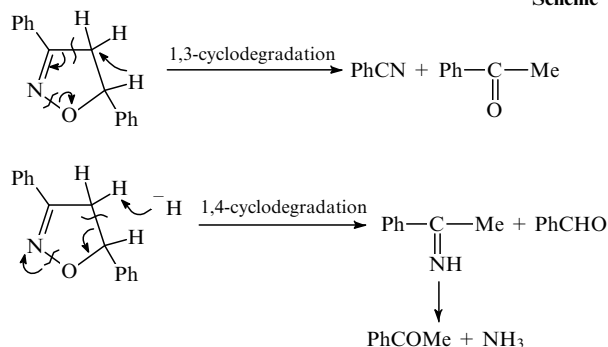
Ar = Ar¹ = Ph: R = R¹ = H (**a**); R = Br, R¹ = H (**b**);
 R = H, R¹ = Me (**c**); R = Me, R¹ = H (**d**);
 R = R¹ = H: Ar = *p*-MeOC₆H₄, Ar¹ = Ph (**e**);
 Ar = Ph, Ar¹ = *p*-MeOC₆H₄ (**f**);
 R = Me, R¹ = H, Ar = Ph, Ar¹ = 2-thienyl (**g**).

Thus, upon heating at 280 °C, the benzalacetophenone oxime **66a** gives 36% of benzonitrile, 30% of acetophenone, 4% of benzaldehyde, 6% of ammonium benzoate, water, and ammonia. At first, 3,5-diphenylisoxazoline **25a** is formed from this oxime at 200 °C; further heating up to 280 °C gives the products of 1,3-(benzonitrile and acetophenone) and 1,4-cyclodegradation (benzaldehyde and acetophenone imine). The latter undergoes easy hydrolysis into acetophenone and ammonia. It is thus supposed that pyrolysis of oximes proceeds through the intermediate formation of isoxazolines with their subsequent cyclodegradation by two pathways. A scheme has been proposed for the 1,3-cycloreversion, which involves a hydride shift. It is believed that 1,4-cyclodegradation is a reductive process consisting in the transfer of the hydride ion; however, the donor of this ion has not been identified (Scheme 7). The isolation of the isoxazoline **67c** in 65% yield and the absence of cyclodegradation products in the pyrolysis of the oxime **66c** are evidence in favour of the proposed mechanism. Probably, in this case the postulated hydride shift is impossible. The reaction with the oxime **66d** gave benzonitrile (50%) and propiophenone (56%), the products of 1,3-cyclodegradation of the intermediate, isoxazoline **67d**, and its aromatisation product, 3,5-diphenyl-4-methylisoxazole. There was no 1,4-cyclodegradation under these conditions.

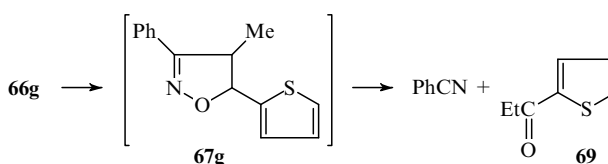
By analogy with the behaviour of other five-membered heterocyclic systems, the authors assumed that the both pathways of cyclodegradation (1,3 and 1,4) are cases of retro-1,3-dipolar cycloaddition. However, the dipolar ion, ⁺CH₂–CH(Ph)–O[–], formed upon 1,3-cyclodegradation, is devoid of the four π-electrons in the C–C–O bond system necessary for its conversion into an alternative canonical structure, [–]CH₂–CH(Ph)–O⁺, while in the case of the vinylnitrene **68**, the original product of 1,4-cycloreversion, such an isomerisation is very likely:



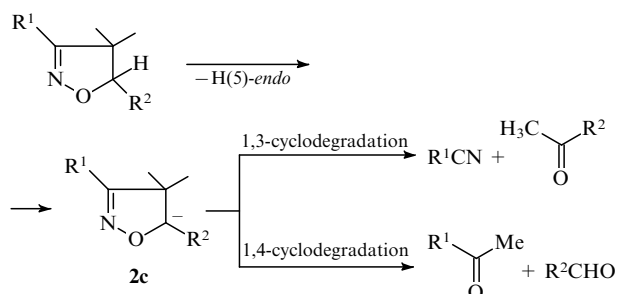
Scheme 7



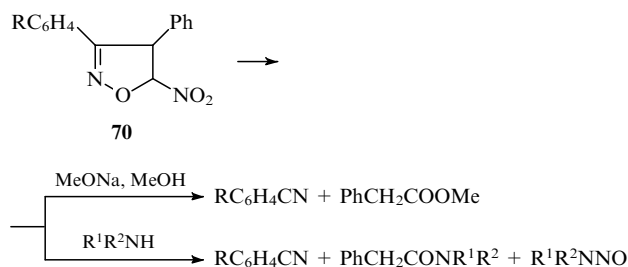
For 2-methyl-1-phenyl-3-(2-thienyl)prop-2-en-1-one oxime **66g**, the corresponding intermediate product, isoxazoline **67g**, could not be isolated under the conditions of thermal cyclisation,⁴⁰ apparently due to the high susceptibility of the latter to cyclodegradation. This reaction gave only benzonitrile and the corresponding ketone **69**.



It should be noted that benzonitrile oxide and alkene, the products of cycloreversion by the third possible pathway (the so-called ‘3,5-retro-Grünanger addition’), were not identified among the products of oxime pyrolysis. Such a process did not take place in other cases either. Obviously, this process is hardly likely due to the energy gain in the direct reaction. Studies of the interaction of 3-substituted isoxazolines with bases did reveal cases of 1,3-cycloreversion. 1,3-Cycloreversion of isoxazolines under the action of bases is associated with the possibility of generating an anion at C(5) of the isoxazoline. It is known that the most acidic protons are the proton at C(3) in 3-nonsubstituted isoxazolines and the proton at C(4) in 3-substituted isoxazolines.^{7, 18} 5-*endo*-Deprotonation is not usual in this case; it can occur only in isoxazoline structures in which deprotonation at other carbon atoms is hindered, on the one hand, and which contain substituents at C(5) able to stabilise the anion formed, on the other hand. Thus, a significant increase in the proton H(5) acidity can be invoked by electron-acceptor substituents at C(5).⁴¹ Indeed, isoxazolines carrying electron-acceptor substituents turned out to be highly susceptible to such a cyclodegradation. The degradation of the cyclic carbanion **2c** generated as a result of C(5) deprotonation by the nucleophile can further proceed in accordance with the scheme:

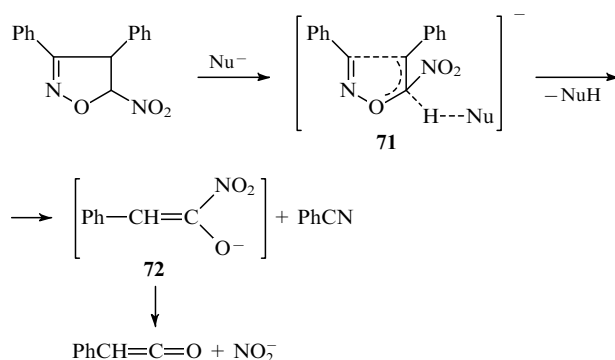


Baranski and Cholewka⁴² observed 1,3-cycloreversion under conditions of the Nef reaction. This is the first example of such reaction. Treatment of 3,4-diaryl-5-nitroisoxazolines **70** with a stoichiometric amount of NaOMe in absolute methanol resulted in the nitrile and methyl phenylacetate; an analogous reaction with Et₃N or cyclic amines in aprotic solvents results in the nitrile and the corresponding amides.⁴²



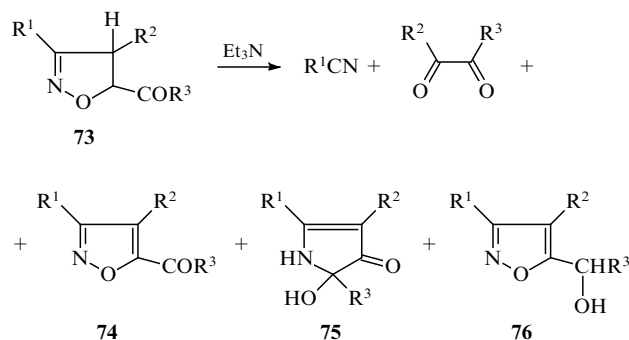
Since it had been known that 5-nitroisoxazolines easily eliminate nitrous acid to give the corresponding isoxazoles^{43–46} (see also Section V), it has been postulated that cyclodegradation is preceded by the aromatisation of the heterocycle through the elimination of nitrous acid. The isoxazoles formed thereby can undergo further degradation by the nucleophile. However, the composition of the reaction products excluded the intermediate formation of isoxazoles. Furthermore, unlike 4-nitro-2-isoxazolines, 5-nitroisoxazolines were not subjected to aromatisation by MnO_2 .⁴⁷

The most likely mechanism of the 1,3-cycloreversion of nitroisoxazolines is believed to be the synchronous E_2 -process with transfer of the H(5) proton to the nucleophile, the cleavage of the N–O and C(3)–C(4) bonds in the intermediate **71**, and the changes in the order of the C=N and C(4)–C(5) bonds. Further transformations of the acyclic anion **72** consist in the elimination of the nitrite anion and the formation of ketene.⁴²



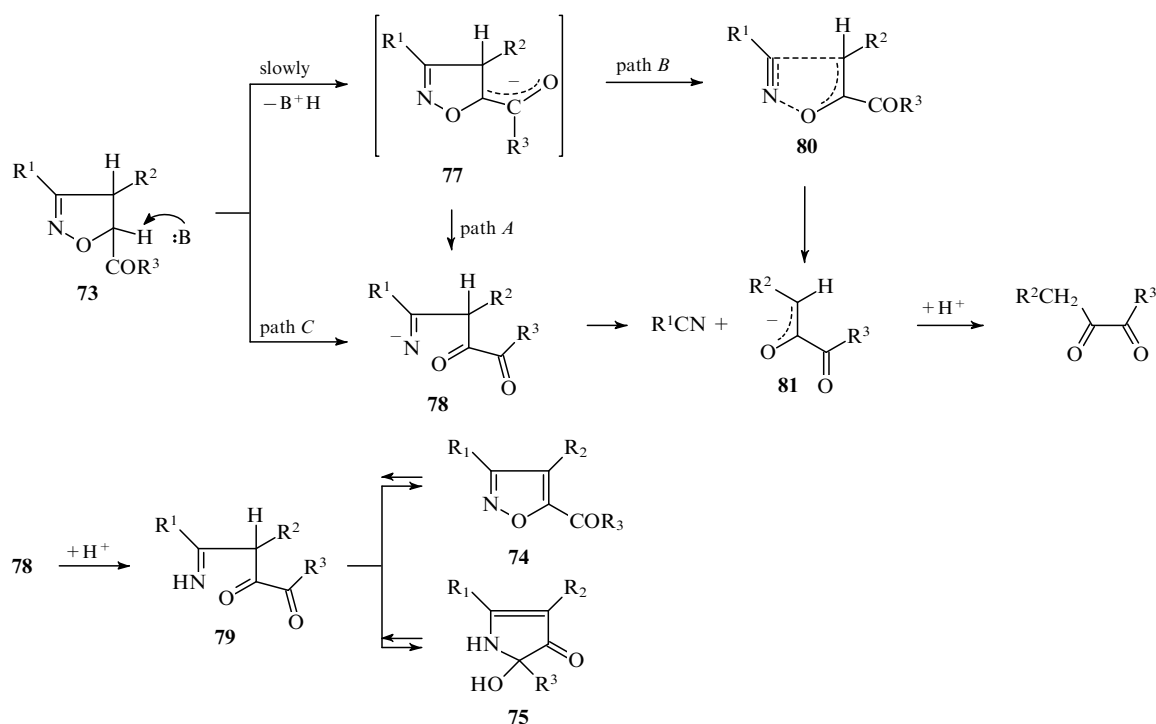
It has to be noted that a final choice in favour of one of the proposed alternative mechanisms is difficult to make, because it is not easy to draw a demarcation line between the ability of 5-nitroisoxazolines for aromatisation and their susceptibility to cyclodegradation. Apparently, aromatisation and cyclodegradation are competing processes, and the composition of the products is determined by both the particular structure of the substrate and the nature of the nucleophile used.

The 5-acylisoxazolines **73**, which decompose into nitriles, α -diketones, isoxazoles **74** and **76**, as well as Δ^2 -pyrrolin-4-ones **75** under the action of bases, are also susceptible to C(5)-deprotonation.^{41, 48} 5,5-Disubstituted isoxazolines are stable under these conditions due to the impossibility of C(5)-deprotonation.⁴¹



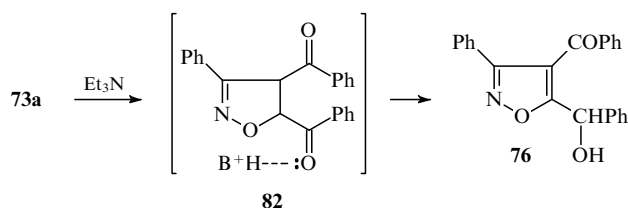
In methanol, C(5)-deprotonation of 5-acylisoxazolines **73** gives approximately 8% of the isoxazoles **74** and **75**, whereas in benzene their yield is as high as 70%. The mechanism of formation of 5-hydroxy-2-pyrrolin-4-one **75** can be represented by Scheme 8. In the presence of bases, C(5) deprotonation of isoxazoline **73** occurs with the formation of the anion **77**; this is followed by its cleavage at the N–O bond to the anion **78** and reprotonation give the equilibrium mixture $\text{74} \rightleftharpoons \text{79} \rightleftharpoons \text{75}$. The fragmentation products, the nitrile and the α -diketone, form by the same scheme either by pathway *A* or *B*. Pathway *A* seems to be more preferable than pathway *B*, for it includes a symmetrical cycloreversion via the activated complex **80**. However, it is difficult to make a choice between these pathways, since both of the corresponding transition states for **78** and **80** have similar energy.⁴⁸

Scheme 8

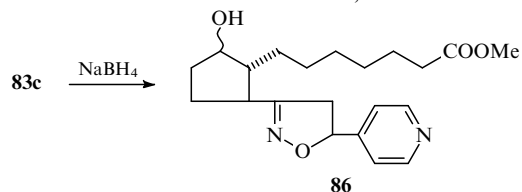
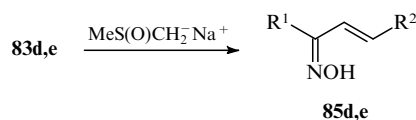
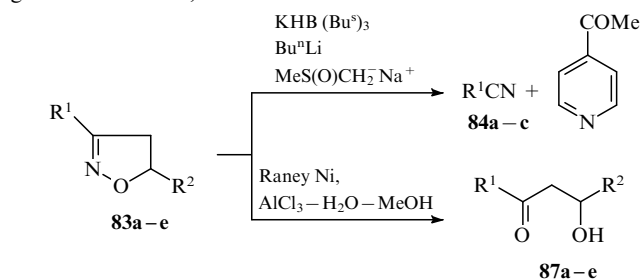


No deuterium exchange occurs on addition of triethylamine to a solution of isoxazolines **73** in D₂O (¹H NMR data); therefore it can be suggested that the equilibrium $73 \rightleftharpoons 77$ does not exist and deprotonation is the slowest stage of the process. The lack of direct evidence for the formation of the anion **77** allows one to suggest that degradation via pathway *C* is not unlikely. On the other hand, ignoring pathway *B* and considering pathway *A* to be the only one possible, the degradation of the isoxazoline ring to the imino diketone **79** must be more effective in benzene than in methanol, since the transition complex **78** contains a contact ion pair with triethylamine (Scheme 8).

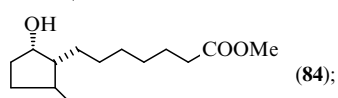
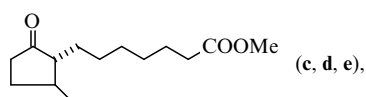
In conformity with this assumption, the formation in a high yield of the isoxazole **76** upon the cyclodegradation of 4,5-dibenzoyl-3-phenyl-2-isoxazoline (**73a**) ($R^1 = R^3 = \text{Ph}$, $R^2 = \text{COPh}$) in the reaction with triethylamine can best be explained by the transition state **82**.⁴⁸



1,3-Cycloreversion of the 3-R-5-(4-pyridyl)isoxazolines **83a–c** resulting in the nitriles **84a–c** and 4-acetylpyridine occurs on the interaction of these isoxazolines with bases (butyllithium and dimsylsodium) and potassium selectride,^{49,50} whereas their analogues **83d,e** interact in accordance with the known schemes to give enoximes **85d,e**.^{2,3,15,51}



$R^1 = -\text{C}_6\text{H}_3(\text{OMe})_2$ (a), $-(\text{CH}_2)_4\text{COOMe}$ (b),

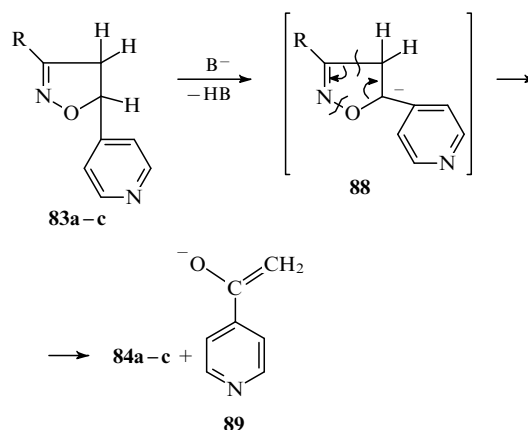


$R^2 = \text{pyridyl-4}$ (a–c), Ph (d), $-\text{CH}_2\text{OPh}$ (e).

It is noteworthy that the reduction of the isoxazoline **83c** with sodium tetrahydroborate results in the formation of the carbonyl-group reduction product, **86**. Upon reductive cleavage (Raney Ni, AlCl_3 , $\text{MeOH}-\text{H}_2\text{O}$), 5-pyridylisoxazolines **83a–c** and 5-phenyl(phenoxymethyl)isoxazolines **83d,e** give the β -hydroxy ketones **87**, which is typical of isoxazoline cleavage by reagents of this type.^{1,3}

The formation of different products in the reaction with nucleophilic agents from the 5-pyridylisoxazolines **83a–c** and from the 5-phenylisoxazolines **83d,e** points to the involvement of the substituent at C(5). In the case of the derivatives **83a–c**, the products of the cyclodegradation of the isoxazoline fragment form, and the ketone-nitrile 1,3-cycloreversion of 5-(4-pyridyl)-2-isoxazolines observed is similar to the cycloreversion of 5-acyl- and 5-nitro-2-isoxazolines and seems to proceed in accordance with Scheme 9:

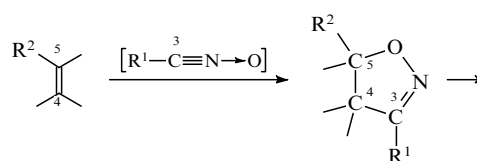
Scheme 9

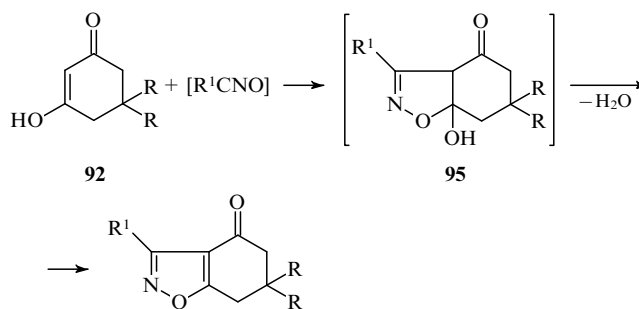
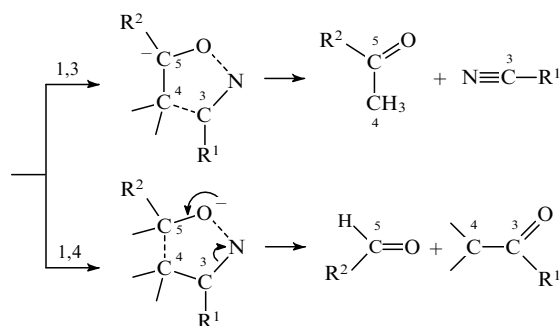


The first step in the 1,3-cyclodegradation of 5-pyridyl-2-isoxazolines **83a–c** is the generation of the anion **88** under the action of the base. Subsequent redistribution of the electron density in the isoxazoline fragment results in the cleavage of the N–O and C(3)–C(4) bonds. The formation of a stable molecule of the corresponding nitrile **84** from the N–C(3)–R fragment is the driving force of this cyclodegradation. The C(4)–C(5)–O fragment carrying originally a negative charge undergoes cyclodegradation to give the enolate anion **89** and then acetylpyridine. It should be noted that all the cases of 1,3-cycloreversion observed previously in reactions with bases seem to occur with the participation of the isoxazolinium anion, the stabilisation pathways of which depend on the specific reaction conditions and the reagents used.

The interaction of the compounds **83d,e** with butyllithium and dimsylsodium occurs via the intermediate formation of the anion of the **2b** type (see Section II), which, depending on conditions, can regenerate the original isoxazoline (BuLi , -78°C) or can be cleaved at the C(5)–O bond to form the stable enoxime **85** (dimsylsodium, 20°C).

It should be noted in conclusion that the sequence: $[2+3]$ -cycloaddition $\rightleftharpoons$ deprotonation $\rightleftharpoons$ $[2+3]$ -cycloreversion is a potentially promising method for the oxidative cleavage of the double bond with simultaneous elongation of the carbon chain at its ends (the so-called method of 'indirect carbolytic cleavage of the double bond').^{52,53}



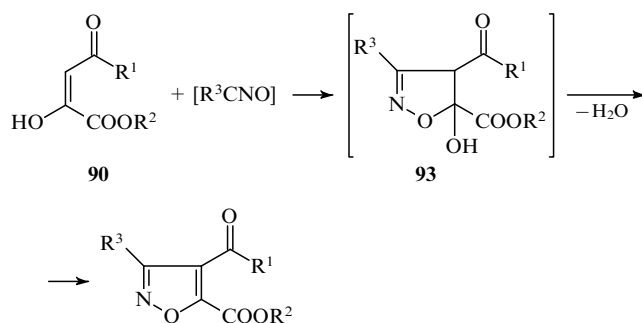


R = H, Me; R¹ = Alk, Ar.^{56,57}

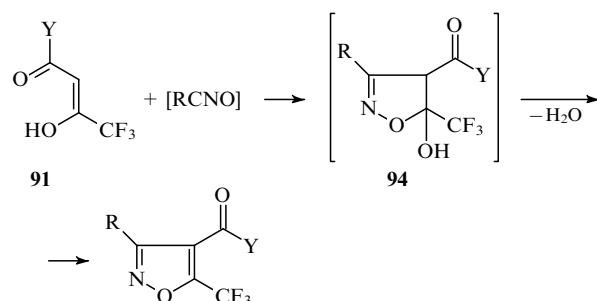
V. Aromatisation of 2-isoxazolines

The tendency toward the formation or elongation of a system of conjugated bonds via the formation of a heteroaromatic ring can be one of the reasons for the conversion of isoxazolines into isoxazoles. Another reason for such conversions is, as a rule, the presence in one of the positions of the carbon skeleton of the isoxazoline heterocycle of a substituent which represents a 'good leaving' group. These substituents can be eliminated spontaneously in the course of isoxazoline formation or under the action of reagents stimulating the elimination process.

Thus, aromatisation of isoxazolines into the corresponding isoxazoles is often observed in the reaction of 1,3-dipolar cycloaddition of nitrile oxides to enones, 1,3-diones, and their derivatives.^{54–59} Aromatisation of the cycloadducts formed as a result of the addition of the nitrile oxide dipole at the double bond of the enolic form of the β-dicarbonyl compounds **90**–**92** occurs via the elimination of the water molecule from the intermediate 5-hydroxy-2-isoxazolines of the **93**–**95** type.

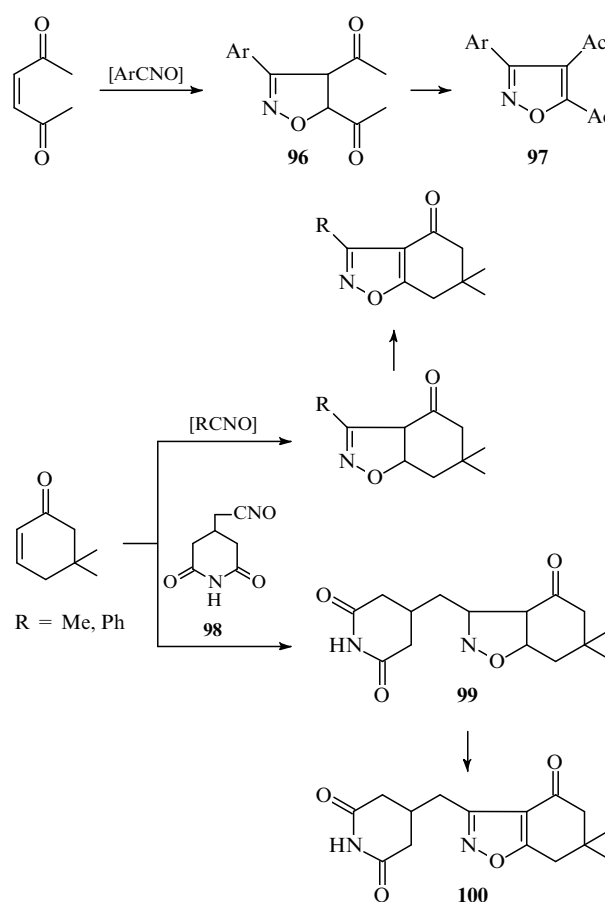


R¹ = Me; R² = Me, Et;
R³ = Ph, C₆H₄NO₂, C(O)Me, COOEt, C(O)Ph.⁵⁴



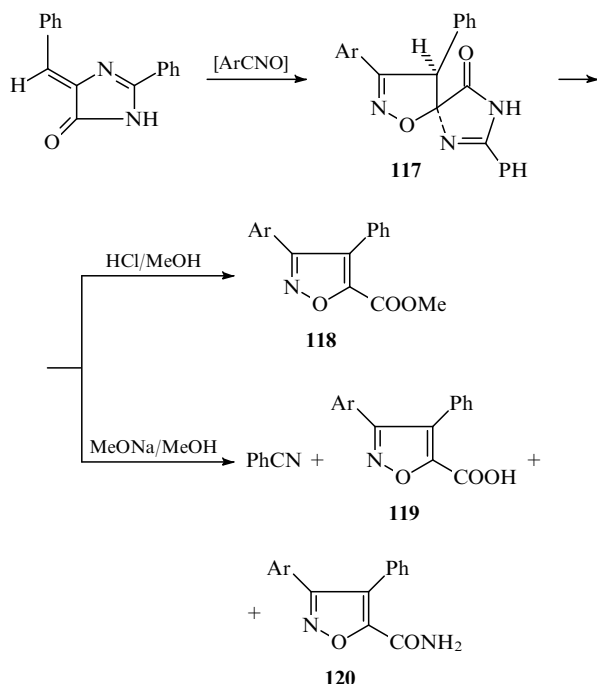
Y = OAlk, Ar, thienyl-2; R = Alk, Ar.⁵⁵

Aromatisation of cycloadducts with enones is a result of an oxidative transformation.^{58,59} One can assume that the aromatisation of 4,5-diacetyl-2-isoxazoline **96** into 4,5-diacetylisoxazole **97** occurs via an identical mechanism.⁶⁰ The reaction of the nitrile oxide **98** with 5,5-dimethylcyclohex-2-enone gives the isoxazoline **99**; however, it is readily converted into the corresponding isoxazole **100** during purification on a column or on boiling in *tert*-butyl alcohol in the presence of chloranil.^{61,62}

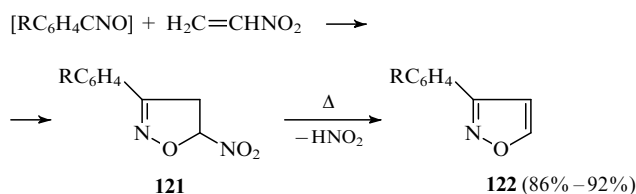


The ease of elimination of the substituent at C(5) of isoxazoline is not only due to the effect of the reaction medium, but also due to the presence of such good leaving groups as acyloxy, alkoxy, and amino groups. Thus, an attempt to synthesise the isoxazoline **101** from the corresponding enone and nitrile oxide has led to the 5-acylisoxazole **102**.⁶³

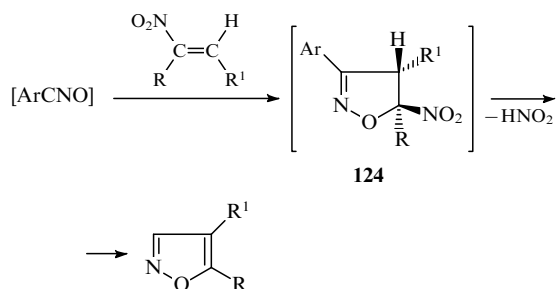
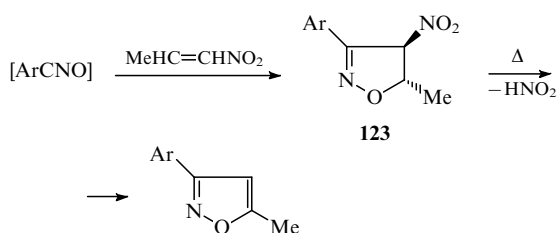
silica gel, did not react with nucleophilic reagents, but readily converted into the isoxazoles **118**–**120** upon acid or alkaline hydrolysis. In this particular case, the aromatisation of the isoxazoline **117** occurs through the elimination of the lactam ring fragments formed upon the hydrolytic cleavage of the azlactone substituent at C(5).⁶⁸



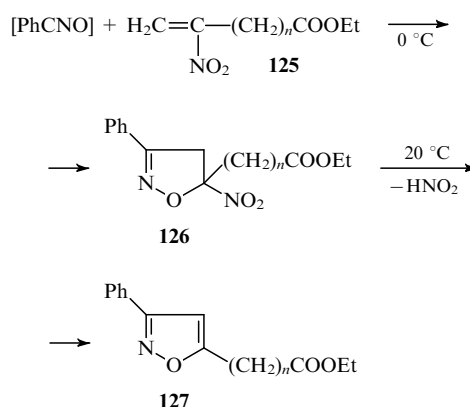
The instability of 4- and 5-nitro-2-isoxazolines was repeatedly observed in their synthesis from nitrile oxides and nitroalkenes, when the primary product of the cycloaddition, the corresponding 2-isoxazoline, converted into the isoxazole with elimination of nitrous acid.⁴⁶ Some nitroisoxazolines formed in this reaction are rather stable under reaction conditions; however, they undergo rapid aromatisation on heating. Thus, the interaction of aromatic nitrile oxides with nitroethylene resulted in the 5-nitro-2-isoxazolines **121**, which on boiling in toluene gave high yields of the isoxazoles **122**.^{43,44}



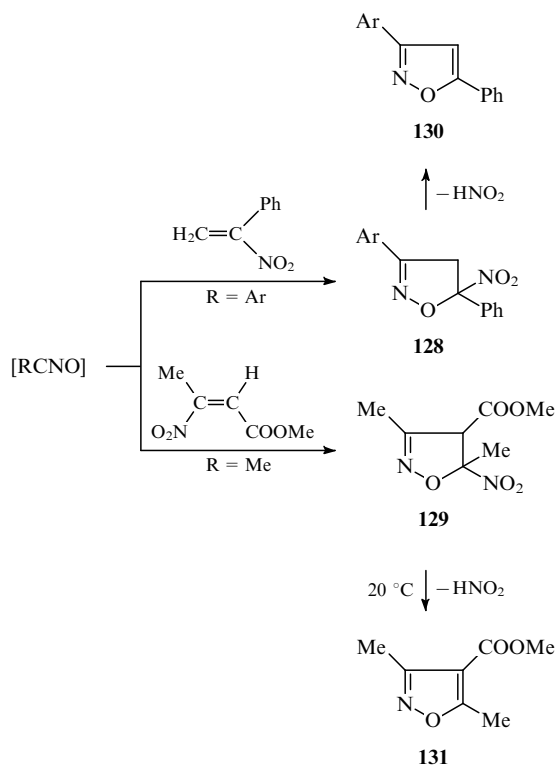
The ability to eliminate nitrous acid differs for various substituted 4- and 5-nitroisoxazolines. Thus, 4-nitro-5-methylisoxazolines **123** aromatised upon prolonged heating, whereas the derivatives of 5-nitro-2-isoxazoline **124** aromatised spontaneously under reaction conditions.^{45,46}



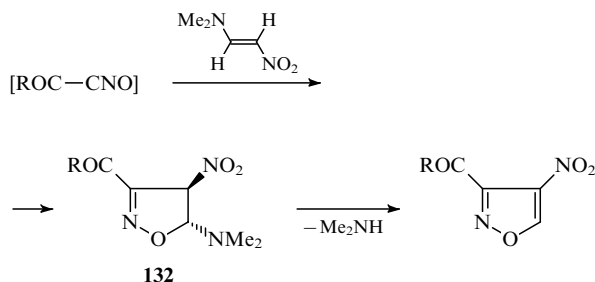
The 1,3-dipolar cycloaddition of benzonitrile oxide to α -substituted nitroethylenes of the type **125** at 0 °C gives the isoxazolines **126**, which spontaneously convert at 20 °C into the isoxazoles **127** with the elimination of the nitro group.⁶⁹



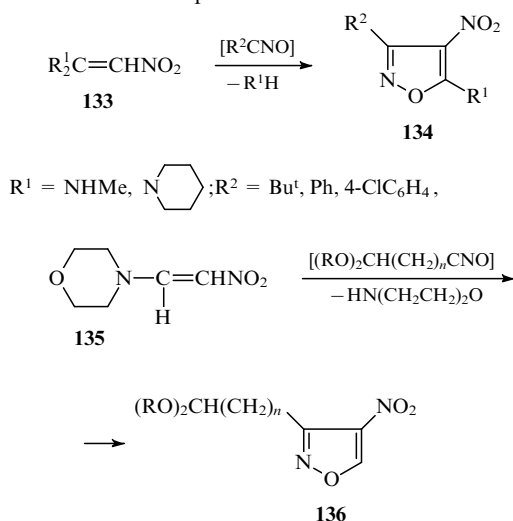
The nitro group can be eliminated more readily from isoxazolines than the cyano and carboxy groups.^{70,71} Thus, the nitro group eliminates preferentially from C(5) of the 5-nitro-5-alkyl(aryl)isoxazolines **128** and **129** to give the corresponding 3,5-diaryl- (**130**)⁷² or 3,5-dialkylisoxazoles (**131**).^{72,73}



However, if the isoxazoline contains an amino group as in the case of 4-nitro-5-dimethylaminoisoxazoline **132**, it is this group that is eliminated during aromatisation.^{74,75}

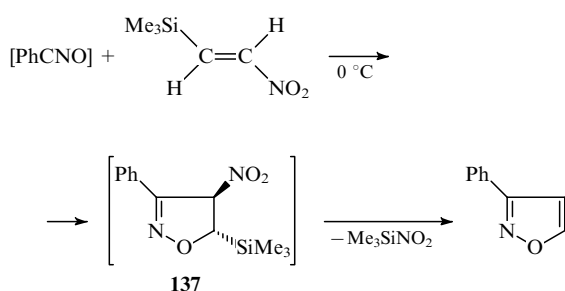


The reactions of the β,β -diaminonitroethylenes **133** with nitrile oxides give the 5-amino-4-nitro-3-isoxazoles **134**, the products of elimination of one of amine molecules.⁷⁶ In the case of the 1,3-dipolar cycloaddition of the nitrile oxide to the nitroalkene **135**, the isoxazole **136** is also formed as a result of preferential elimination of morpholine.⁷⁴



The adducts of benzonitrile oxide with halonitroethylenes aromatise to give 4- and 5-nitroisoxazoles which can be explained by the ability of intermediate isoxazolines to eliminate the hydrogen halide molecule more readily than HNO_2 .⁴⁶ It should be noted that spontaneous elimination of hydrogen halide under conditions of nitrile oxide synthesis was often observed when halogenoalkenes were used as dipolarophiles.^{57,77} Hence, in some cases unstable 4- and 5-nitroisoxazoles can be obtained by cycloaddition to nitroalkenes containing a substituent group, which eliminates more readily than the nitro group.⁴⁶

The nitro group can be split off, not as nitrous acid, but as a stable compound with another substituent in the isoxazoline ring. Such an ability for elimination is useful in the synthesis of some isoxazoles. For example, in the synthesis of 3-phenylisoxazole by the nitrile oxide method, the substituents at C(4) and C(5) eliminate simultaneously from the isoxazoline **137** formed in the first stage of the reaction:⁷⁸



According to their ability for cleavage, the 2-isoxazoline substituents can be arranged in the following order: $\text{NR}_2 > \text{Hal}, \text{OR} > \text{NO}_2 > \text{CN}, \text{COOR}$.

Aromatisation of isoxazolines was observed either under conditions of nitrile oxide synthesis or under the action of reagents (predominantly acidic). Spontaneous aromatisation of isoxazolines formed as intermediate adducts of the nitrile oxide synthesis occurs with the participation of bases and if C(5) contains hydrogen, which is readily cleaved by bases. Aromatisation of amino-substituted isoxazolines occurs, as a rule, under conditions of proton catalysis.

As noted above, aromatisation of some 5-substituted isoxazolines is a very likely reason for the formation of unusual degradation products upon interaction with metal polycarbonyls (see Section III). Thus, the formation of enamino ketones upon treatment of isoxazolines with iron or molybdenum polycarbonyls^{34,39} apparently involves elimination of 5-acyloxy-, 5-ethoxy-groups, or 5-pyrrolidinyl substituents, since the corresponding hydroxy ketones must be the normal products of cleavage of the N—O bonds of isoxazolines.

The competing process of aromatisation is the reason for the conversion of 5-aminoisoxazolines into enamino ketones, the aromatisation being the major pathway in the interaction of isoxazolines with molybdenum hexacarbonyl. The tendency to aromatisation is also realised for 4,5-diacylisoxazolines. Their reactions with bases give isoxazoles in addition to 1,3-cyclodegradation products (see Section IV). In this case, aromatisation is the result of hydride shifts occurring with the participation of acyl substituents or it is analogous to the oxidative transformations of the adducts of the nitrile oxide synthesis.

The examples considered above provide evidence for the competition of the aromatisation of the isoxazolines with the reactions of 1,4- or 1,3-cyclodegradation, which is particularly true for the isoxazoline derivatives carrying good leaving groups as substituents.

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Acylation of acetals and related geminal systems. The use of this reaction in the synthesis of phospholipids

E E Nifant'ev, D A Predvoditelev

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Abstract. The practical significance of acylation of acetals, orthoesters, and their aza-analogues (oxazolines) in fine organic synthesis is considered. Attention is mainly focused on the application of this reaction to the design of glycerophosphatides and other types of phospholipids. The use of acylation of these geminal alkoxides and oxazolines makes it possible to optimise the strategy of the synthesis of polyfunctional ester systems. The bibliography includes 76 references.

I. Introduction

Acetals,[†] orthoesters, and other geminal alkoxides are of special interest as stable derivatives of the corresponding carbonyl compounds, which are formed at certain stages of synthetic schemes.^{1–3} In addition, they are used as effective donors of α -substituted carbocations in the formation of carbon–carbon^{1,4,5} or carbon–hydrogen^{6,7} bonds in the design of complex polyfunctional systems. In all these cases, the alkoxide fragment of the above-mentioned compounds as synthetic material is partly or completely lost.

At the same time, geminal alkoxides can also function as synthetically useful derivatives of polyhydric alcohols. This possibility was established as early as the last century, but has been introduced into routine preparative practice only in recent years. The main attention was focused on the conversion of cyclic acetals of polyhydric alcohols into complex lipids. The main results of these investigations are discussed in the present review.

II. Acetals as nucleophiles

The simplest and functionalised acetals can react with phosphorus and sulfur halides as well as with phosgene to give the corresponding α -haloethers.^{1,8,9} The mechanism of these reactions has not

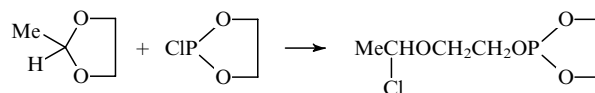
[†] We use the term 'acetals' to denote geminal alkoxide derivatives of aldehydes and ketones.

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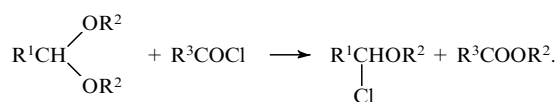
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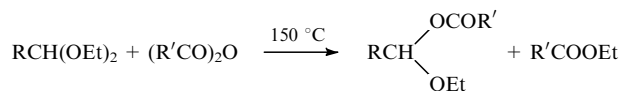
been studied in detail. However, it presumably involves an electrophilic attack of the acetal oxygen by phosphorus, sulfur, or carbon to give oxonium compounds, which are transformed into α -haloethers, either directly or via several stages. Simultaneously, the eliminated alkoxy group is converted either into halophosphite (phosphate), -sulfite (sulfate), or -carbonate or into the corresponding alkyl halides. This rationalisation of the chemical nature of this process has been substantiated by studies of the interaction of acetaldehyde ethylene acetal with ethylene chlorophosphite.¹⁰



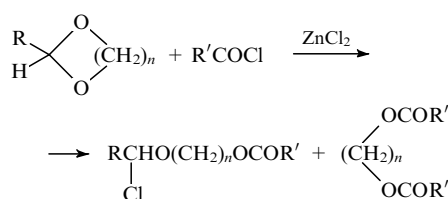
The interaction of acyclic acetals with the simplest carboxylic acid halides in the presence of Lewis acids, which also results in α -haloethers, has been reported.^{11–16}



Similarly, C–O bond cleavage occurs when acetals react with anhydrides (as had been shown long ago by Claisen¹⁷).¹⁸

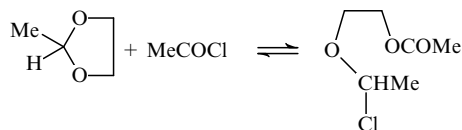


The above reactions have also been studied in relation to cyclic acetals, 1,3-dioxolanes and 1,3-dioxanes. It has been established that acylation of cyclic compounds is a complex process, which normally gives a mixture of products.^{19–26}



$n = 2, 3.$

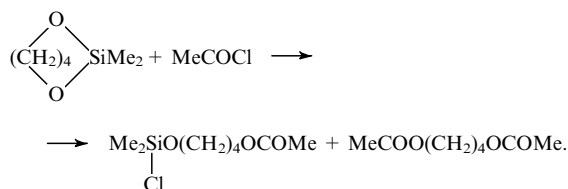
In some experiments it has been shown that ω -acyloxyalkyl chloroalkyl ethers tend to cyclise, which leads to establishment of an equilibrium, for example:²³



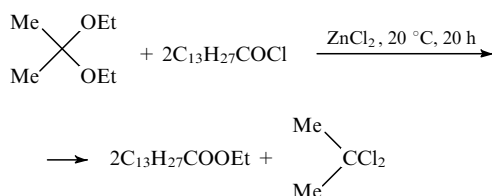
In addition, dehydrochlorination of these α -chloroethers has been observed.¹⁰

Acylation of ethylidene derivatives of monosaccharides with acetic anhydride in the presence of trifluoroacetic acid with subsequent hydrolysis of the acylal-acetal formed initially has been proposed by Kochetkov et al.²⁷ as a method for removing acetal protection.

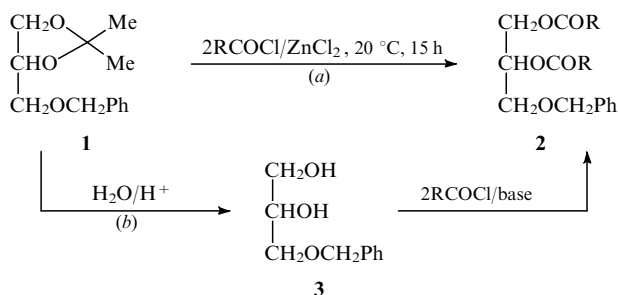
This reaction was further extended to acylation of silicon analogues of cyclic acetals, 1,3,2-dioxasilacyclanes. These compounds react with acid halides to give mono- and di-acylation products.²⁸



It can be concluded that in the studies on acylation of acetals with chlorides and anhydrides of simplest carboxylic acids, interesting chemical phenomena have been observed but no new preparative methods for organic synthesis have been developed. These methods were elaborated later in studies of the reactions of acetals with chlorides of higher fatty acids in the presence of zinc chloride or other Lewis acids, for example, of the reaction of acetone diethyl acetal with myristoyl chloride.²⁹



A version of this reaction that consists in acylation of cyclic acetals is of great preparative importance. This method was used, in particular, to obtain 1,2-di-*O*-acyl-3-*O*-benzylglycerols **2**, which are important intermediates in the chemistry of lipids, based on accessible 1,2-*O*-isopropylidene-3-*O*-benzylglycerol **1** (pathway *a*).^{29,30} The acetal **1** has been traditionally employed in lipid syntheses: it was hydrolysed to the diol **3**; the latter was isolated and purified and then acylated to give the final esters **2** (pathway *b*). This synthesis required large amounts of solvents and additional reagents. The yield of the ester **2** was as low as 40%–45% with respect to the initial acetal **1**.³¹

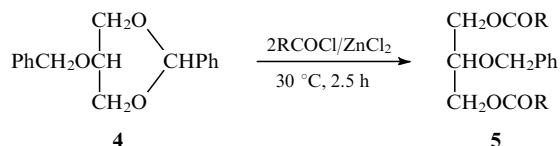


R = C₁₅H₃₁, C₁₇H₃₅.

A new synthetic method consisting in direct acylation of the acetal **1** is much more simple and efficient, and the yields of the esters **2** obtained in this way reach 65%. This reaction is usually carried out in a small amount of ether or chloroform or without solvents.

An increase in the acylation temperature to 60 °C decreases the yields of the glycerides **2** due to partial debenzylation. It is significant that the glycerides **2** are formed not only when two moles of acid chloride per mole of the acetal **1** are used, but also at an equimolar ratio of the reagents. However, in the latter case, about half of the initial acetal does not react.^{29,30} ‡

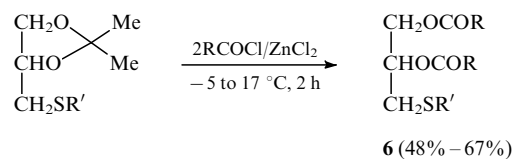
Complete acylation of acetals can also be used for the conversion of 1,3-dioxanes, e.g. 1,3-*O*-benzylidene-2-*O*-benzylglycerol **4**, into the corresponding esters **5**.^{30,32}



R = C₁₅H₃₁, C₁₇H₃₅.

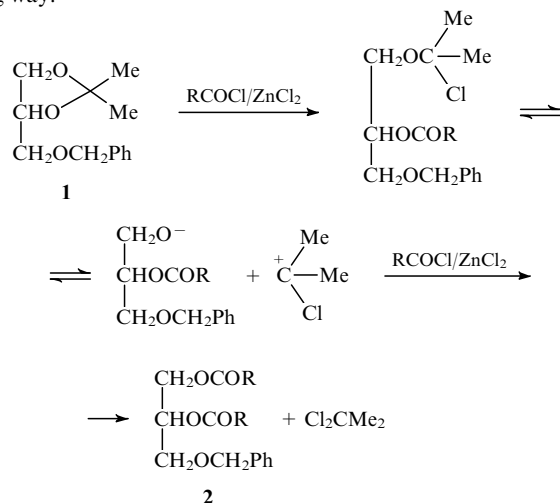
The isomeric glycerides **2** and **5** were investigated by high-resolution NMR spectroscopy. It was noted that no acyl migration along the glycerol system occurred during the synthesis.³² Thus, the practical utility of this method for target-directed syntheses of more complex lipids was demonstrated.

This method was also used in the synthesis of other natural systems such as diacyl derivatives of *S*-alkylthioglycerol **6**.³³



R = C₁₅H₃₁, C₁₇H₃₅; R' = C₁₆H₃₃, C₁₈H₃₇.

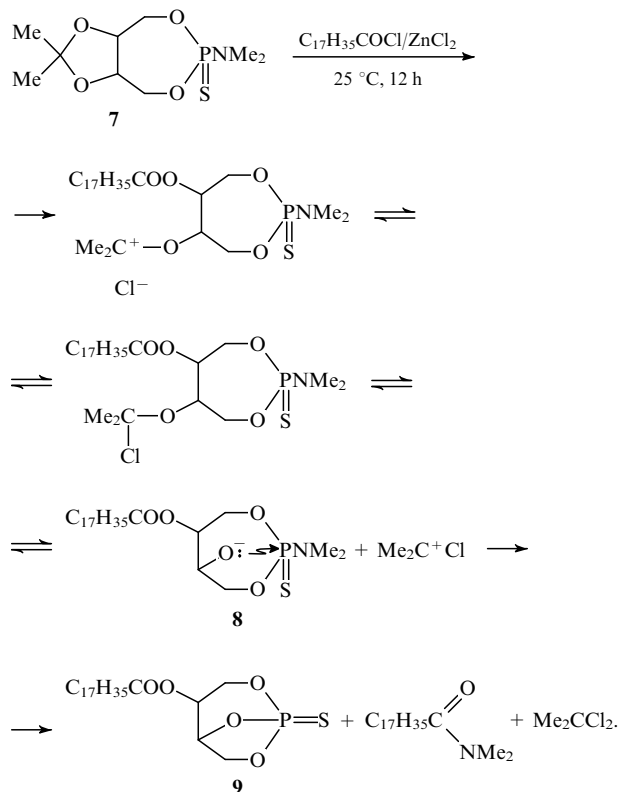
Complete acylation of the cyclic acetal **1** appears to be a two-stage process, which can be schematically presented in the following way:³⁰



The isolation of 2,2-dichloropropane is evidence in favour of this mechanism. In addition, to confirm the above mechanism, a model acetal was specially 'designed'; its structure was to ensure

‡ The benzylacetal **1** can also be converted into the ester **2** by treatment with carboxylic acids in the presence of *p*-toluenesulfonic acid. However, in a preparative sense, this procedure is more complex because it requires heating to 110 °C and removal of the H₂O and acetone formed in the process.³⁰

that the negatively charged oxygen atom (if it was generated at the first stage of acylation) comes close to the electrophile. The electrophile should 'trap' the alkoxy-anionic centre thus preventing diacylation. For this purpose, 2-dimethylamido-5,6-isopropylidenedioxy-2-thiono-1,3,2-dioxaphosphepane **7** was used as the model compound. At the first step of acylation, this compound generates alkoxy anion **8**, which, due to the proximity to the dimethylamidothiophosphoryl group, effectively interacts with it by a nucleophilic substitution mechanism. As a result, no second acylation takes place and the phosphorus framework compound **9** is formed instead of the diacylate:^{34, 35}

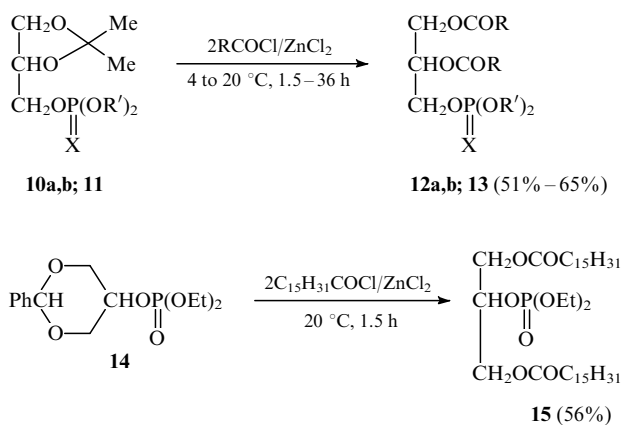


Orthoesters and other geminal alkoxydes are also nucleophilic and susceptible to acylation. In the studies of these compounds, some interesting chemical features have been found. Therefore, their acylation will be considered separately in the foregoing sections.

III. Synthesis of phospholipids based on glycerol acetals

Complete acylation of acetals has been investigated most extensively and thoroughly in connection with the synthesis of glycerophospholipids and their analogues. 1,2-*O*-Isopropylidene- or 1,3-*O*-benzylideneglycerols were used in these studies as the initial compounds; they were consecutively introduced into phosphorylation, direct acylation, and subsequent auxiliary transformations of the polar fragments of the molecules. It was found that acylation of phosphorylated acetals, occurring under mild conditions corresponding to the acylation of the simplest cyclic acetals, is effective, and has a broad range of synthetic applications. It is noteworthy that acylation of glycerol acetals was studied in parallel with the development of new methods for the design of a lipid-phosphorus unit.^{36, 37} These two lines of research successfully complemented each other and greatly contributed to progress in the synthetic chemistry of phosphoglycerides.

Let us consider acylation of glycerol acetals aimed at the synthesis of phosphatidic acids and their thio- and seleno-analogues. This task can be solved using accessible compounds, such as acetal phosphates **10a, b, 14** and thionophosphates **11a** as initial substances.^{29, 30, 32, 38}



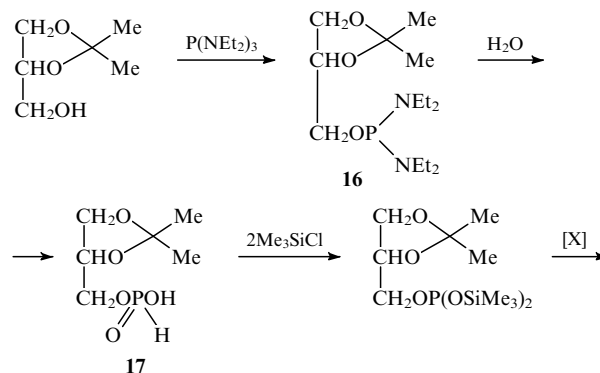
R' = Et (**10a, 11, 12a, 13**), Ph (**10b, 12b**); X = O (**10, 12**), S (**11, 13**).

An increase in the molar amount of the acid chloride (more than 2 moles per mole of the acetal **10a**) has no substantial influence on the yield of the phosphates **12a**. An increase in the reaction temperature (> 50–60 °C) results in the formation of various side products. For example, in the case of the acetal **10a**, considerable amounts of ethyl carboxylates are formed, while the acetal **10b** gives 1,2-di-*O*-acyl-3-chloro-3-deoxyglycerols.³⁰

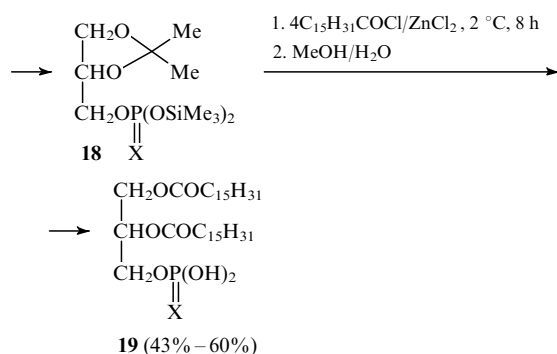
In order to elucidate whether migration is possible during the acylation, the chromatographic mobility and ¹H, ¹³C, and ³¹P NMR spectra of ethyl esters of α-phosphatidic acid **12a** and of its β-isomer **15** have been analysed. From chromatographic and spectral data it was concluded that acyl migration did not occur during the synthesis.³²

The phosphates **12a** and **15** and thionophosphates **13** obtained were transformed into phosphatidic acids **19** and their thiono-analogues; first, they were made to react with Me₃SiX and then the silyl derivatives thus formed were hydrolysed.^{29, 30, 32, 38}

An alternative method for preparing the phosphatidic acids **19** is acylation of the glycerophosphate silyl ester acetal **18**. In this case, the synthetic scheme involves preparation of amidophosphites of 1,2-*O*-isopropylideneglycerol **16**, their hydrolysis to primary phosphites **17**,⁸ and silylation of the latter. This is followed by oxidation or addition of sulfur (selenium), acylation, and desilylation.^{39, 40}



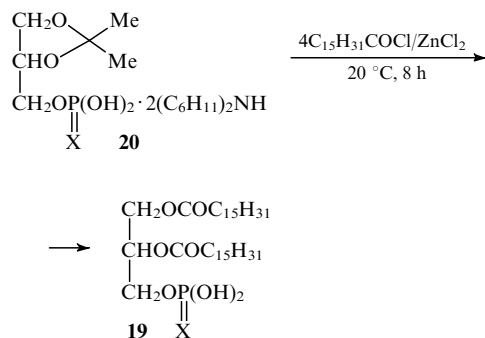
§ These compounds are often called *H*-phosphonates, which is not, in our opinion, a very adequate term.



X = O, S, Se.

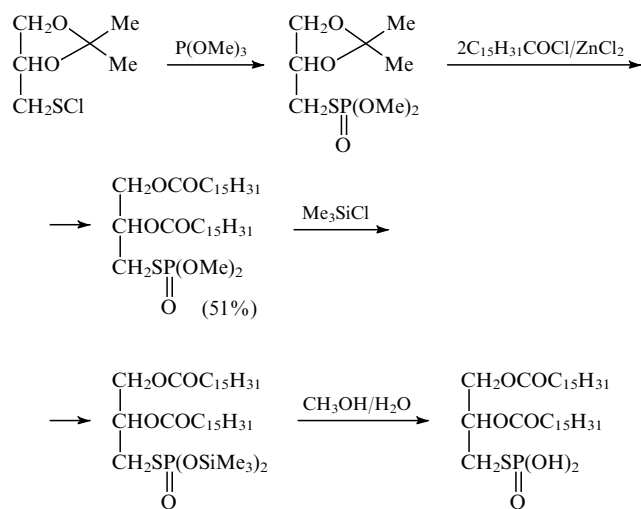
In this case, as in those described above, the efficiency of acylation was found to be higher for thione derivatives than for selenone derivatives. Using the latter synthetic scheme, an optically active phosphatidic acid, 1,2-di-*O*-palmitoyl-*sn*-glycero-3-phosphate, was obtained. The synthesis was not accompanied by changes in the chirality of the glycerol system.³⁹

If required, phosphatidic acids and their thione analogues **19** can be obtained by acylation of salts of 1,2-*O*-isopropylidene-glycero-3-phosphates **20**.^{39, 40}



X = O, S.

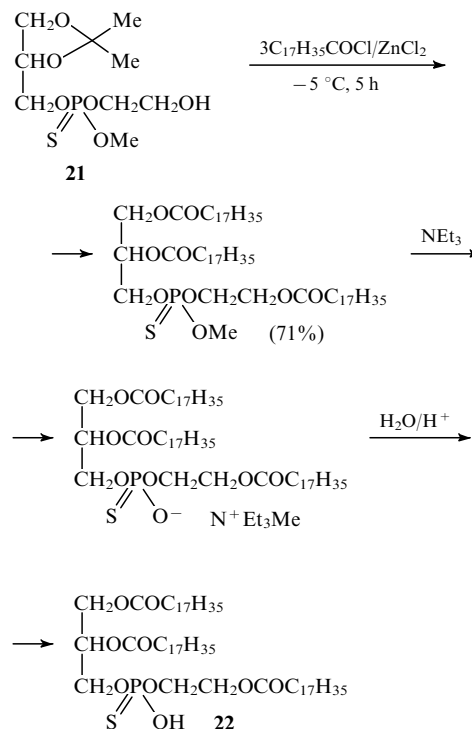
In recent years, enzymological demands have stimulated studies of thiol analogues of natural phosphate systems. Derivatives of this kind of the series of phosphatidic acids were obtained by an elegant procedure.⁴¹



Another trend in phospholipid synthesis involving acylation of acetals is the design of natural esters of phosphatidic acids and their S-analogues. For this purpose, a preparative scheme has

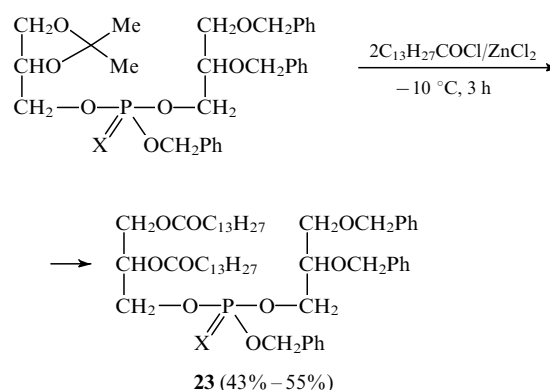
been developed, which includes the initial formation of glycerol acetals with protected phosphate groups. These phosphorylated acetals are first acylated and then deprotected. Methyl, ethyl, and benzyl groups are used most frequently as protective groups in these syntheses.

The synthesis of thionophosphatidyl acyl glycols of type **22** can serve as an example.⁴²



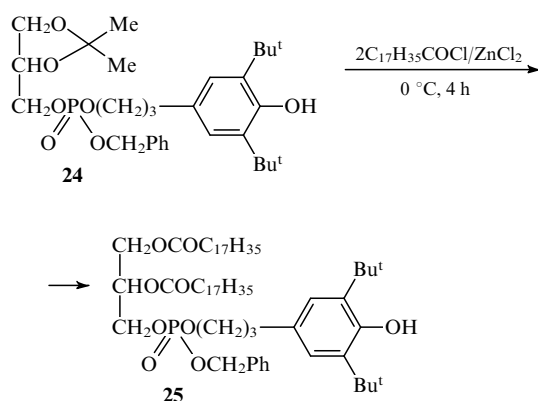
Acylation of the phosphatoacetal **21** was carried out with a threefold molar excess of palmitoyl chloride; therefore, both the acetal group and the alcohol hydroxyl underwent acylation.

The synthesis of phosphatidyl ethylene glycol systems **22** was supplemented by the synthesis of phosphatidyl glycerol derivatives **23**. A simple method that proved to be effective was used for this purpose.⁴³



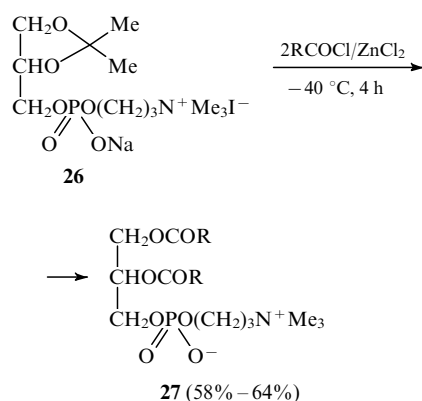
X = O, S.

Glycerophosphates with a protected phosphate group were also used to produce membrane-directed antioxidants by chemical combination of phosphatidic acids and sterically hindered phenols. In fact, phosphatidyl ionols **25** containing 4- γ -oxypropyl-2,6-di(*tert*-butyl)phenol as the protective moiety were obtained by acylation of the acetal **24** with stearoyl chloride.⁴⁴



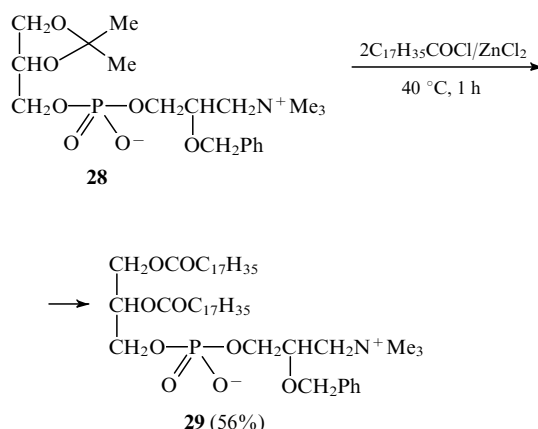
It should be noted that the acylation does not affect the sterically hindered phenolic hydroxyl.

Synthesis of lipid phosphodiester by acylation of glycerol acetals can also be performed without protection of the free phosphate hydroxyl. For example, the phosphatidyl homocholines **27** have been effectively prepared by acylation of the sodium salt of the glycerol homocholine phosphate **26**.⁴⁵

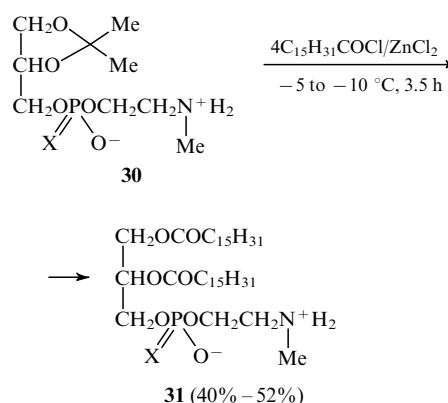


R = C₁₅H₃₁, C₁₇H₃₅.

More complex lecithin derivatives **29** containing a hydroxy-homocholine residue were also synthesised by acylation of the phosphoacetals of type **28**.⁴⁶

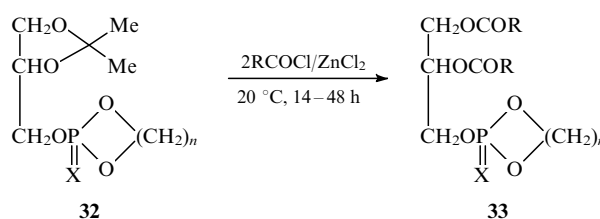


Acylation was also used in the synthesis of phosphatidyl-*N*-methylethanolamines and their thione analogues **31**.⁴⁷ For this purpose, *N*-methylaminoethyl phosphate **30** was treated with an excess of palmitoyl chloride. It is noteworthy that this reaction does not involve *N*-acylation.



X = O, S.

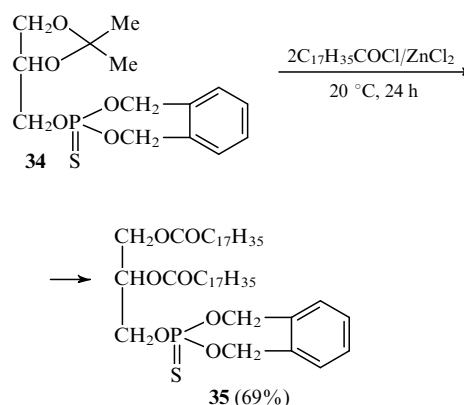
Acylation of compounds containing phospho-rings (these compounds play a significant role in the synthetic chemistry of phospholipids) constitutes a special line of research.³⁷ For example, acylation of acetals containing six- and seven-membered rings with phosphoryl, thiophosphoryl, and selenophosphoryl groups has been carried out.^{48–51}



X = O, S, Se; *n* = 3, 4; R = C₁₅H₃₁, C₁₇H₃₅.

It should be emphasised that acylation was not accompanied by opening of the phospho-rings. The yields of the target products **33** depended on the ring size; for phosphorinanes they reached 68%, whereas for simplest phosphhepanes, they were only 25%–58%.

Fused phosphhepanes appeared to be more convenient starting compounds than their monocyclic analogues **32**. For example, phosphhepane **34** is readily and effectively converted into the lipid system **35**.⁵²

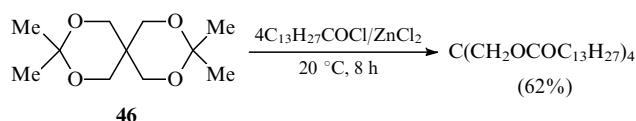
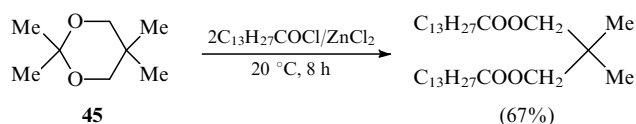


Acylation of systems **36** the rings of which contain sulfur or selenium atoms, in addition to phosphorus and oxygen atoms, has also been studied.⁴⁹ The yields of the target products **37** in this reaction were relatively low (45%–47%), which may be due to the partial acylation of the sulfide or selenide centres in the initial phosphates **36**.

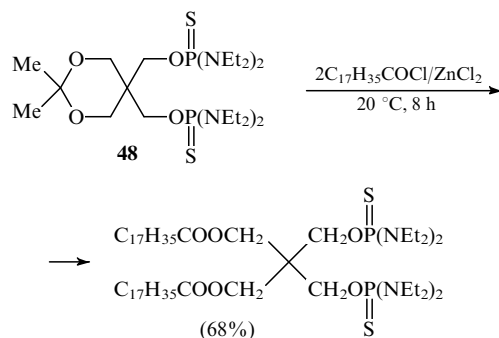
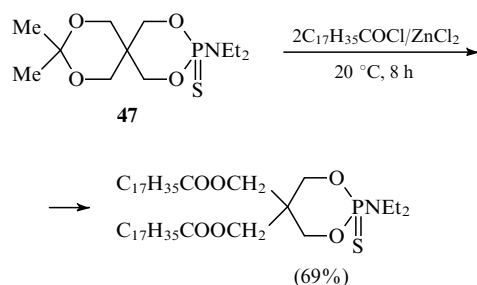
V. Synthesis of phospholipids based on acetals of tri- and tetramethylolalkanes

In modern lipidology, a new trend has appeared, devoted to the study of systems derived from unusual polyhydric alcohols. Acylphosphopentaerythritols and related compounds belong to this group. Acylation of mono- and diacetals of oligomethylolalkanes has been widely used in the synthesis of these lipids.

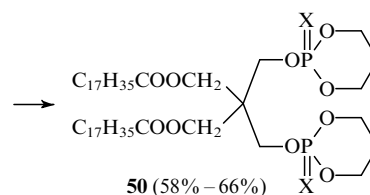
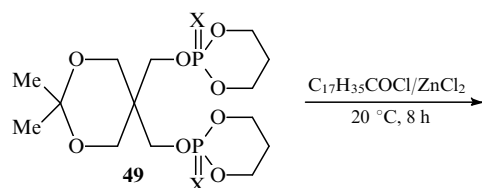
The design of new phospholipids was preceded by studies on acylation of model systems **45** and **46** based on 2,2-dimethyl-1,3-dioxane. It was shown that the mono- and diacetals **45** and **46** are smoothly and effectively acylated, according to the method described above.^{55,56}



It was then demonstrated that mono- **47** and dithiophosphamide **48** acetals of pentaerythritol are acylated with an equal efficiency.^{55,56}



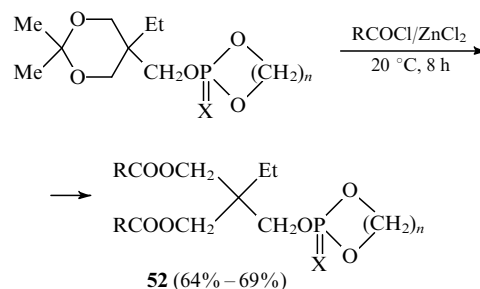
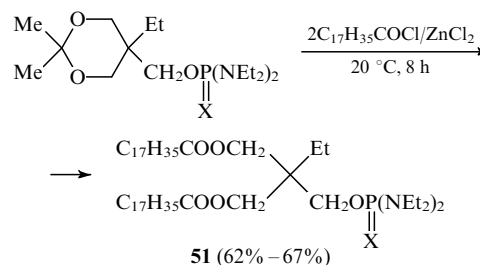
To obtain bis(dioxaphosphorinane) derivatives of diacylpentaerythritol **50**, the corresponding acetals **49** were introduced into the reaction with stearoyl chloride under standard conditions.^{55,56}



X = O, S.

The distearoyl bisphosphates **50** possess an important structural feature: they contain two phosphopropylene rings. This permits these compounds to be used in the synthesis of phospholipids containing two hydrophilic residues in their molecules.^{55,56} In recent years, lipids of this type with enriched hydrophilic fragments have attracted attention of investigators due to their peculiar behaviour in some enzymic reactions⁵⁷ and in membrane modification⁵⁸⁻⁶⁰ and also due to the prospects for their clinical application.⁶¹

The acylation reactions considered above have also been extended to the synthesis of erythritol phospholipids of the amidophosphite **51** and phosphate types **52**.⁶²



X = O, S, Se; $n = 2, 3$; R = C₁₅H₃₁, C₁₇H₃₅.

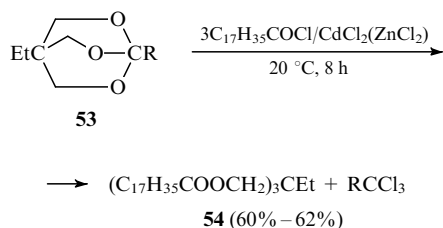
It is noteworthy that the efficiency of acylation in the case of phosphoryl, thionophosphoryl, and selenophosphoryl derivatives of erythritol is virtually identical. In this respect, trimethylol phospholipids differ from glycerophospholipids.

VI. Synthesis of phospholipids based on orthoesters

Orthoesters are classical reagents for fine organic synthesis, which are widely used in preparative practice, especially in the synthesis of heterocyclic compounds. As a rule, their transformations are associated with the formation of stabilised carbocations that are attacked by nucleophiles.^{2,3,5} The reactions of orthoesters with electrophiles have received much less attention.

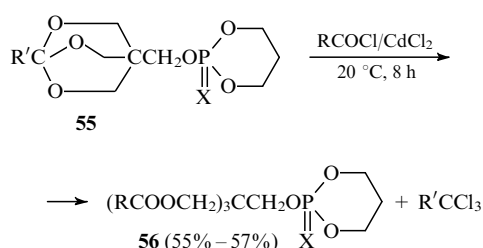
The interaction of orthoesters with phosphorus and sulfur halides resulting in esters of the corresponding mineral acids has been reported.⁶³⁻⁶⁵ Reactions of orthoesters with carboxylic acids, their anhydrides, acyl chlorides, and acyl cyanides have also been described.⁶⁶⁻⁷⁰ These reactions give mixtures of esters and other products. For example, mixing of ethyl orthoformate and acetyl chloride at 20 °C results in ethyl formate, ethyl acetate, and ethyl chloride.⁶³ The use of chlorides of higher fatty acids in acylation has led to similar results.⁷¹

The interaction of acid chlorides with bicyclic orthoesters **53** proceeds in a different way; In this case, complete acylation occurs to give triesters **54**.⁷¹



R = H, Me.

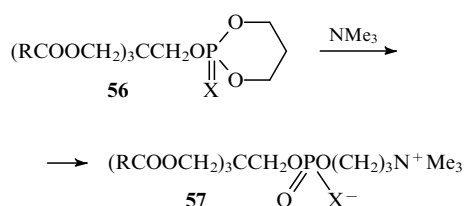
This reaction has been used in the total synthesis of pentaerythritol homocholine phospholipids. To this end, phosphorylated bicyclic orthoesters **55** were converted into triacylphosphates **56** by direct acylation with palmitoyl and stearoyl chlorides.⁷¹



R' = H, Me; X = O, S; R = C₁₅H₃₁, C₁₇H₃₅.

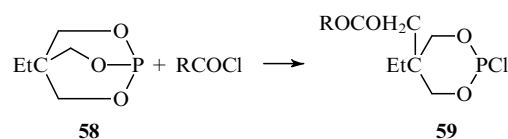
It has been expedient to include this reaction in the scheme of the synthesis of phospholipids, because, in this case there is no need to protect three alcoholic hydroxyls prior to phosphorylation of pentaerythritol and to remove protective groups after phosphorylation.

This reaction has a wide range of synthetic applications, since both phosphate and thiophosphate compounds successfully enter into it. Its practical utility becomes even more evident from the fact that the cyclic phosphates **56** formed proved to be effective alkylating agents. Owing to this property, they were used for obtaining previously unknown pentaerythritol homocholines **57**.⁷¹



X = O, S; R = C₁₅H₃₁, C₁₇H₃₅.

Like bicyclic orthoesters of carboxylic acids, the corresponding orthoesters of phosphorous acid (bicyclic phosphites) **58** also undergo acylation. Here the electrophilic reagent attacks the oxygen atoms rather than the phosphorus atom as could be expected for an Arbuzov reaction.⁷²



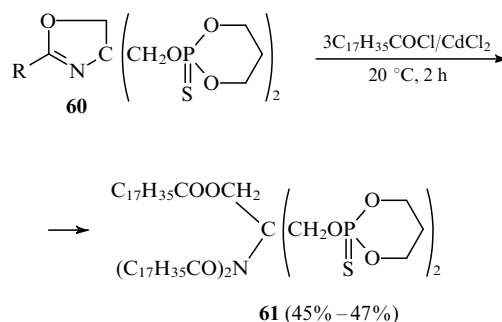
R = CH₃, C₁₅H₃₁, C₁₇H₃₅.

A specific feature of the bicyclic phosphites **58** is their relative inertness in acylation in which only one acyl group is introduced into their molecules.

The resulting cyclic chlorophosphites **59** were used in the syntheses of various lipid-like compounds and other products.⁷²

VII. Synthesis of phospholipids based on oxazolines

Further extension of studies on the acylation of geminal systems has led to the involvement in this process of oxazolines, which had been barely regarded as nucleophiles before.^{3,63} Recently, it has been shown that these accessible and convenient compounds interact specifically with higher carboxylic acid chlorides to yield new types of nitrogenous phospholipids. For example, the reaction of cyclic bis(thiophosphates) of the oxazoline series **60** with stearoyl chloride gave the product of extensive acylation **61**.⁷³



R = H, Me.

In this case, as well as the oxygen atoms of the oxazolines, the nitrogen atoms were also attacked by the electrophilic acylating agent. This reaction is also unique, because it occurs as double *N*-acylation.

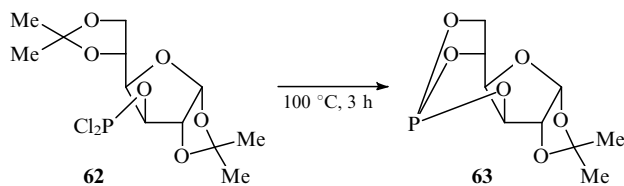
It should be noted that in early syntheses of *N*-monoacyl analogues of glycerophosphocholines based on D- and L-serines with the use of oxazoline protection, the introduction of fatty acid residues into lipid molecules has been carried out in two stages: deprotection in a strongly acidic medium and acylation of the amino alcohols formed with acid chlorides, anhydrides, or esters.^{74,75} The new reaction of direct acylation of oxazolines has broadened considerably the potentialities of phospholipid synthesis.

VIII. Conclusion

The main conclusion of the present review is that a new method of *O*- and *N*-acylation has been added to the arsenal of fine organic synthesis; this method can be applied to the design of lipids and other complex polyfunctional systems. The method is facile and is therefore promising. At the same time, it has a number of specific features as regards the design of synthetic schemes; in particular, it may exclude the stage of obtaining intermediate polyhydroxylic structures.

Studies of the acylation of acetals have been mostly carried out in relation to the synthesis of carboxylic acid esters. Meanwhile, this reaction is also promising for the synthesis of phosphorous acid esters and, obviously, of other types of esters. We have already mentioned the interaction of 1,3-dioxolanes with ethylene chlorophosphite, which occurs as *O*-phosphorylation of the cyclic acetal.¹⁰ Recent studies have demonstrated the possibility of conducting related phosphorylation. It is the intramolecular cyclisation of acetals **62**, the molecules of which contain a dichlorophosphite group.⁷⁶

This simple reaction is a convenient method for the synthesis of framework bicyclic phosphites of carbohydrates **63**.



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The synthesis and properties of interstitial phase films

R A Andrievskii

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Abstract. The methods of synthesis of interstitial phase films (transition metal carbide, nitride, boride, and hydride films) are described. Different versions of their chemical and physical deposition from the gas phase are compared and discussed. The available information about the structures, electronic structures, and physicochemical properties of the films (including alloyed and multilayer films) is surveyed and analysed. The bibliography includes 225 references.

I. Introduction

The term 'interstitial phases' (IP) (or interstitial alloys, interstitial compounds, and Hagg's phases) appeared more than 60 years ago in studies of the structures of the phases in transition metal–light nonmetallic element (hydrogen, nitrogen, boron, carbon, etc.) systems. Hagg¹ put forward the hypothesis that the small atoms of the light elements are inserted in the interatomic sites within typical close-packed metallic structures: face-centred cubic (FCC), hexagonal close-packed (HCP), and body-centred cubic (BCC).

The structures of typical IP of the NaCl type, in which the octahedral positions in the metallic FCC sublattice are occupied by carbon or nitrogen atoms, and of the CaF₂ type, in which the hydrogen atoms are located in tetrahedral positions of the FCC lattice, are well known from the results of neutron diffraction studies.² The structures of the borides are somewhat more complex in most cases than those of the hydrides, carbides, and nitrides, but the familiar simple relations, proposed by Hagg and based on a purely geometrical approach, proved suitable only for stoichiometric phases. Deviation from stoichiometry led in the vast majority of cases to the ordering of the nonmetallic sublattice and the formation of IP with a complex structure, the metallic sublattice of which was no longer in any way characterised by simple FCC, HCP, or BCC type packing. For this reason, as has been emphasised in the monograph of the present author and Umanskii,² the term 'interstitial phases' is mainly of historical significance. At the present time the IP include Group III–VI

transition metal hydrides, nitrides, carbides, and borides with metal-like properties, as well as certain monoxides (for example, TiO). A series of monographs (see, for example, Refs 2–21) and a multiplicity of communications have been published in collections and numerous periodicals devoted to the problems of the preparation, properties and applications of IP. However, questions concerning films have been described in the monograph literature on a very limited scale — so far as we are aware, only in a single monograph.⁷ This situation is due to the fact that IP films began to be actively investigated only during the last 10–15 years after the development of an effective method for their preparation by physical deposition from the gas phase (the so called PVD technology), although chemical deposition from the gas phase (the CVD technology) had long been known. The extensive application of such films in the tool industry and in electronics stimulated the study of the characteristic features of their synthesis and properties. As regards the number of publications, titanium nitride is the undoubted leader. In this connection, one should note the reviews^{22–28} and certain monographs on films and coatings.^{29–31} The available information on nitride, boride, carbide, and hydride films is scattered in the periodical literature and needs to be surveyed. We may also note that this problem appears of current interest also in connection with the development of studies on IP-based nanocrystalline materials.^{32, 33}

II. Preparation

We shall consider films with a thickness up to several micrometers. Thicker films and coatings will not as a rule be analysed. Table 1 presents the principal methods of preparation of IP films. The classification presented is arbitrary because, for example, many physical methods include chemical reactions and chemical procedures have been stimulated by physical influences.³² The table includes only the principal methods of synthesis (vaporisation and condensation processes in an inert medium or in the reaction medium are usually implied). Nitride films can be obtained by virtually all methods, while hydride films can be prepared only by the low-temperature methods in view of the considerable dissociation pressures of the hydrides. The carbide and boride films occupy an intermediate position.

1. Physical methods

a. Thermal evaporation

In connection with the high melting points of the majority of carbides, nitrides, and borides, the processes involving evaporation by resistive or radiation-induced heating are used compara-

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Table 1. Principal methods of preparation of IP films.

Method	Principal varieties	Compound
Physical methods		
Thermal evaporation	Activated reactive evaporation	Nitrides and carbides
	Electron-beam heating	Borides and carbides
	Laser treatment	Nitrides and carbides
Ion plating	Ion arc sputtering	Nitrides and carbides
	Magnetron sputtering	Nitrides, borides, carbides and hydrides
	Ion-beam treatment; implantation	Nitrides and borides
Chemical methods		
Deposition from gas phase	Plasma-associated and plasma-activated CVD processes; electron cyclotron resonance	Nitrides, carbides, and borides
Thermal decomposition	Gaseous and condensed precursors	Nitrides and borides
Nitridation and hydridation	Low-temperature version; implantation	Nitrides and hydrides

tively rarely. Electron-beam evaporation (EBE) has been used to obtain carbide, boride, and carbidoboride (TiC/TiB₂) films.³⁴ This method has been used with heating of the substrates to high temperatures (650–1600 °C); the rate of deposition was up to 6 µm min⁻¹ and the thickness of the layers was 0.25–0.3 mm, but their hardness was relatively low (up to 20–30 GPa) owing to intense recrystallisation. Laser evaporation (LE) is also used.

The thermal vaporisation of metals and alloys in a reaction medium with simultaneous saturation by the interstitial elements (carburation, nitridation and hydridation) is more common. A version of this method — activated reactive evaporation (ARE) — is particularly well known, although the latter is ‘akin’ to ion deposition processes. Laser reactive sputtering of niobium targets in carbon-containing media for the preparation of superconducting niobium carbide films has been described.³⁵ The use of a glow discharge and of other plasma-activating processes for these purposes is known,³⁶ but the most effective variety of the ARE is arc vapour ion deposition (sputtering) (AVID).

In order to obtain IP films by the thermal vaporisation method, account must be taken of the characteristic features of this process. The compounds from which films are obtained possess in most cases wide ranges of homogeneity and vaporise predominantly (at least in the initial stage) incongruently. The possibilities of statistical-thermodynamic methods, which make it possible to estimate the rates of vaporisation and the congruently vaporising IP compositions have been examined in monographs.^{2, 19}

The vacuum vaporisation of intermetallic compounds of the type FeTi and LaNi₅ with subsequent hydridation (VViH) is also used to obtain hydride films (see, for example, Singh et al.³⁷ and Li and Cheng³⁸).

b. Ion plating

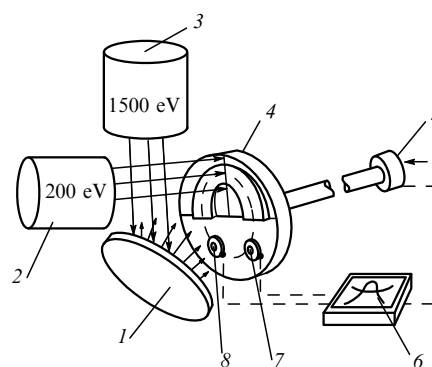
The term ‘ion plating’ was first encountered in the communication of Mattox and McDonald³⁹ for the designation of a wide range of plasma-activated PVD processes in which the surface of the support was subjected to the action of an ion stream before the deposition of the film. The excitation of an arc discharge in a

nitrogen or carbon-containing atmosphere is one of the most common variants of this technology, which has found extensive industrial application (on ‘Bulat’ type devices in our country). Metallic cathodes are used as a source of metal ions in AVID, high degrees of ionisation being attained under these conditions (from 30% to 100%), the kinetic energy of the ions is from 10 to 200 eV, and the rate of deposition may be up to 1–3 µm min⁻¹.^{40, 41}

In most cases Ar + N₂ or Ar + C_nH_m reactive working media at a pressure of ~10⁻³ mm Hg and metallic cathodes (Ti, Ti–Al, Zr, Mo, Cr, etc.) are used in AVID. The principal deficiency of AVID is the formation of the so-called drop phase as a result of the intense influence exerted by the arc on the cathode and the high probability that metal drops enter into the films deposited. Filtered AVID processes, where the drop phase can be to a large extent filtered off by means of a magnetic field, are known.^{24, 42, 43} Also known are hybrid variants of PVD, including both multi-cathode devices and a combination of AVID and magnetron sputtering (MS), which makes it possible to obtain a wide variety of types of multilayer and doped films.⁴⁴

A more flexible variety of ion deposition is MS. In magnetron sputtering, it is possible to employ not only metal and alloy cathodes but also cathodes made of IP as well as nonmetallic compounds and to reduce the temperature of the support to 100–200 °C and sometimes even below that. These factors greatly expand the possibilities for the preparation of films in amorphous and nanocrystalline states and also of supersaturated solid solutions. There are numerous variants of MS: d.c. sputtering, high-frequency sputtering, application of a bias voltage to the substrate, the use of so called unbalanced magnetrons, etc.^{24, 26, 41} However, the degree of ionisation, the kinetic energy of the ions, and the rate of deposition are in almost all cases lower than for AVID (< 10%, up to 10 eV, and < 0.1–0.2 µm min⁻¹ respectively).

Different variants of the ion-beam treatment (IBT), in which atoms are dislodged from the target by the bombardment of its surface with ion beams, have also come to be widely used. The ion beams are also employed for the treatment of the films formed. Figs 1 and 2 present two schemes for the ion-stimulated deposition of nitride films. In the first case, the metal ions are generated by bombarding a metallic target with inert gas or nitrogen ions and in the second a stream of metal atoms is generated by means of an electron-beam treatment.^{45, 46} Such methods make it possible, on the one hand, to synthesise superstoichiometric compounds⁴⁵ and, on the other, to vary the crystallisation conditions. For example, bombardment with heavy ions (320 keV Ar²⁺ or 320 keV Xe²⁺) in the deposition of TiB₂ films leads to the appearance of crystallinity even when the process is carried out

**Figure 1.** Schematic illustration of the binary ion-stimulated deposition of nitride films.⁴⁵

(1) Target (Ti, Zr, Hf); (2) source of nitrogen ions or of a mixture of argon and nitrogen ions for the support; (3) source of argon, xenon, neon, or nitrogen ions for the target; (4) substrate; (5) angular mechanism rotation; (6) coordinate fixer; (7) current density counter; (8) rate of deposition counter.

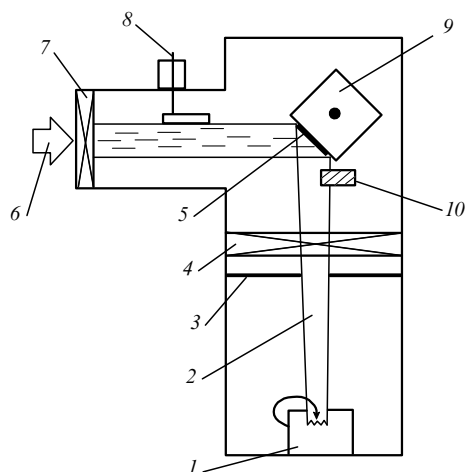


Figure 2. Schematic illustration of the EATON Z-200 IBED apparatus.⁴⁶

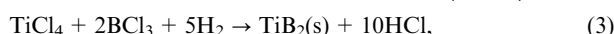
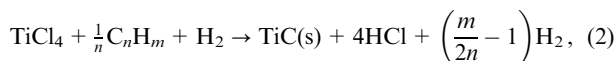
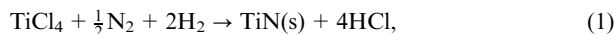
(1) electron-beam vaporiser; (2) stream of vaporised metal atoms; (3) vaporisation lens; (4) separator; (5) substrate; (6) ion beam (N^+ or Ar^+); (7) separator; (8) ion beam current density counter; (9) cooled support holder; (10) rate of deposition counter.

at room temperature.⁴⁷ Only the formation of amorphous films was observed under these conditions without an ion-beam treatment. The use of molecular dynamics methods for IBT processes has been described.⁴⁸

2. Chemical methods

a. Deposition from the gas phase

The traditional CVD technology, associated with high-temperature gas reactions of the type



has long been used to obtain wear-resistant protective layers, films, and general purpose coatings. Reactions (1)–(3) have been formulated in their final form but in fact they consist of many stages and in addition admixtures of oxygen complicate their occurrence in almost all cases. A comprehensive review of the studies devoted to wear-resistant TiN CVD coatings has been published.²⁷ Not only single-layer IP films but also multilayer and doped compositions of the type $Ti(C_xN_y)_z$, $TiC + TiN$, $TiC + Al_2O_3$, $TiC + TiB_2$, and $TiC + Al_2O_3 + TiN$ have been developed and are manufactured on the industrial scale.^{24, 27}

In most cases the temperature range for the deposition of CVD films is 900–1100 °C. Rates of deposition of 0.03–0.2 $\mu m \min^{-1}$ are typical for these conditions. The search for the possibility of reducing the process temperature, dictated mainly by the requirements of electronics and machine building, have led to the creation of different variants of physically stimulated regimes, in which plasma and laser techniques, electron cyclotron resonance (ECR), etc. are used.^{49–54} The following features are characteristic of these variants:

(1) the deposition temperature is reduced to 600–300 °C and below;

(2) the rates of deposition are 0.001–0.2 $\mu m \min^{-1}$;

(3) organometallic precursors of the type of titanium tetrakis[dimethyl (or diethyl) amides] or tetraisopropoxide — $Ti[N(CH_3)_2]_4$, $Ti[N(C_2H_5)_2]_4$ and $Ti[OCH(CH_3)_2]_4$ — having a high vapour pressure are used;

(4) compared with the usual CVD technology, these methods require special apparatus, so that their application is in most cases justified economically only in electronics.

Figure 3 presents a schematic illustration of the apparatus in which titanium tetrakis(dimethylamide) vapour and nitrogen are used and which is activated in an ECR cell.⁵¹ The initial vacuum in the apparatus is maintained with the aid of a turbomolecular pump at a level below 10^{-10} mm Hg, while the working nitrogen pressure is 10^{-4} mm Hg. The temperature of the substrate, on which a shift potential is established, amounts to ~ 100 °C. The highest rates of deposition ($\sim 6 \times 10^{-4} \mu m \min^{-1}$) and comparatively low electrical resistances of the films have been observed when a shift potential of -50 V was applied to the support. The composition of the films, monitored with the aid of XPES, proved to be as follows (at. %): Ti ~ 42 , N ~ 42 , C ~ 10 , O ~ 6 . Other schemes for the employment of ECR in order to obtain TiN films have been described. When these schemes are employed, the impurity content can be reduced by an increase in temperature but the rates of deposition remain nevertheless relatively low ($\sim 10^{-3} \mu m \min^{-1}$).^{52–54}

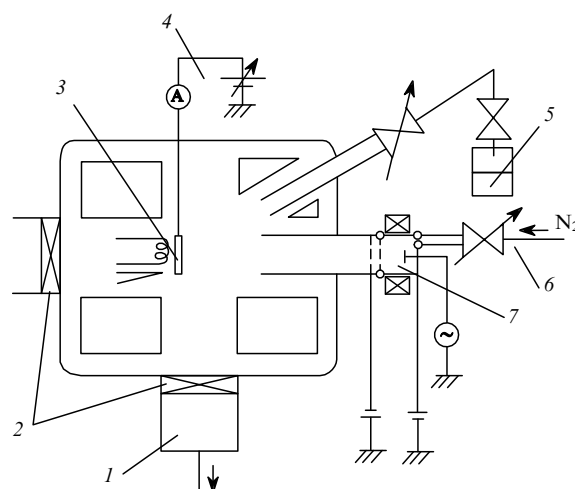


Figure 3. Schematic illustration of the apparatus for the deposition of TiN films using an organometallic precursor and the activation of nitrogen by means of cyclotron resonance.⁵¹

(1) turbomolecular pump; (2) nitrogen traps; (3) substrate with a device for heating and the measurement of temperature; (4) bias voltage source; (5) organometallic precursor ($T = 75$ °C); (6) supply of nitrogen; (7) cell of 90 W cyclotron resonance apparatus with a high-frequency generator and source and mains potential generators.

Examples of the synthesis of films comprising complexes of group IV and V transition metal tetrakis (dialkylamides) and ammonia at atmospheric pressure have been described.^{55, 56} Fairly high rates of deposition (0.02–0.2 $\mu m \min^{-1}$) and low temperatures (200–400 °C) were then noted and the impurity content was low; the formation of TiN , Zr_3N_4 , Hf_3N_4 , VN , Nb_3N_4 , and Ta_3N_5 was detected. Epitaxial layer-by-layer growth of TiN film at 500 °C was observed when $TiCl_4$ and NH_3 were supplied alternately to the support with injection of zinc vapour after the supply of titanium chloride.⁵⁷

It is seen from the foregoing that, in the course of the updating of the regimes in the traditional CVD technology, experimental data have accumulated and new schemes have been tested, but it is so far difficult to give preference to any one of them.

b. Thermal decomposition

The thermolysis of gaseous and condensed precursors for the preparation of IP films is used comparatively rarely. As regards titanium nitride and carbonitride films there have been indications that thermal decomposition of organometallic compounds of the type of titanium tetrakis(dialkylamides), including polymeric ones, is possible without the addition of ammonia to the reaction zone.^{49, 58}

The deposition of titanium, zirconium, and hafnium boride films by the thermolysis of borohydrides has been described in several communications (see, for example, Refs 59–62). At fairly low decomposition temperatures (100–250 °C), the formation of both amorphous and crystalline films with a fairly high metallic conductivity is observed. The latter property is particularly attractive for the employment of these films in electronics as diffusion barriers. However, owing to the high reactivity of borohydrides, so far boride films are obtained by this method mainly on a laboratory scale.

c. Nitridation and hydridation

The nitridation and hydridation methods are applied in different variants: ionic and laser implantation of nitrogen and other interstitial elements in thin metallic films (Figs 1 and 2) or surface layers,^{63–65} nitridation of surface layers in a high-frequency discharge,⁶⁶ high-temperature (400 °C) nitridation by hydrazine,⁶⁷ and hydridation of films at low temperatures including electrochemical and magnetron synthesis.^{37, 38, 60, 69} However, compared with methods for deposition from the gas phase and thermal decomposition, nitridation and hydridation have no special advantages. Hydride films may be an exception, but the characteristic features of their preparation have so far been investigated on a limited scale.

III. Composition, structure, defects, and electronic structure

The thickness of the films determines the application of the corresponding methods for their investigation.⁷⁰ This applies particularly to the study of their decomposition and defectiveness, for which many methods are employed; XPES, XRD, Auger electron spectroscopy (AES), scanning and transmission electron microscopy (SEM, TEM), Rutherford back scattering spectroscopy (RBSS), electron microprobe analysis (EMA), positron annihilation spectroscopy (PAS), secondary ion mass spectrometry (SIMS), scanning tunnelling and atomic force microscopy (STM, AFM), selected area electron diffraction (SAED), and others. In most cases, two and more methods are used to ensure the reliability of the results.

1. Composition

Table 2 presents certain results of the analysis of the composition of IP films obtained by different methods. The formulae of the films, found in a number of investigations,^{51, 52, 54, 60, 72, 75, 76} were calculated by ourselves on the hypothesis that the boron, nitrogen, oxygen, and carbon atoms are located in one sublattice (for example, in octahedral positions), while the smaller hydrogen atoms are in another sublattice (for example, in tetrahedral positions). In many cases, the synthesis of IP films is accompanied by the formation of superstoichiometric compounds. The influence of argon pressure on the boron content in diboride (TiB₂ and ZrB₂), hexaboride [(La, Ce, Sm, Y)B₆], and dodecaboride (ZrB₁₂) films obtained with the aid of MS has been examined.⁷⁷ The formation of superstoichiometric phases in the first two cases and of prestoichiometric phases in the last case was noted. This was attributed to the characteristic features of the mobility and the collision reactions of the boron and metal atoms. The formation of superstoichiometric titanium carbonitrides and boridonitrides with the aid of MS has also been reported.⁷⁸ The important question concerning the relation between the compositions of the target and the sputtered film as regards IP has not so far been considered in detail. It has been noted⁷⁸ that the depletion in carbon of a nonstoichiometric titanium carbide (TiC_{0.5}) target has been detected with the aid of MS.

In the synthesis of the usual IP, the formation of superstoichiometric phases is observed mainly in the presence of oxygen impurities, which leads to the appearance of structural (non-thermal) vacancies in the metallic sublattice.^{2, 7} The insufficiently complete attestation of the compounds listed in Table 2 precludes

Table 2. Compositions of certain IP films synthesised by various methods.

Compound	Method of preparation	Method of analysis	Ref.
NbC _{0.75–0.98}	LRS	XPES	35
Ti(N _{0.72} C _{0.17} O _{0.11}) _{1.38}	ECR	"	51
TiN _{0.74–1.07} H _{0.1–0.42}	"	RBSS	52
Ti(N _{~0.9} C _{0.05} O _{0.03}) _{0.8–1.3} H _{0.1–0.3}	"	SIMS	54
TiN, Zr ₃ N ₄ , Hf ₃ N ₄ , VN _{1.05–1.15} , NbN _{1.35} , TaN _{1.7}	Low-temperature CVD	RBSS, XPES, SAED	55, 56
Zr(B _{0.67} C _{0.17} O _{0.16}) _{2.25}	TD	AES	60
TiN _{1.2} , ZrN _{1.5} , NbN _{0.9} , TaN _{0.8}	Implantation	RBSS, XRD	64
TiN _{0.8–1.2}	DCMRS	RBSS, XPES, SAED, XRD	71
(Ti,Al,Zr)(N _{0.96} O _{0.04}) _{0.96}	"	"	72
TiN _{0.2–1.14}	"	AES	73
TiB _{2.1–2.85}	HFMNS	AES, XRD	74
Zr(N _{0.83} C _{0.13} O _{0.04}) _{~2}	HFMRS	"	75
Ti(B _{0.8} O _{0.11} N _{0.045} C _{0.045}) _{2.5}	HFMNS	AES	76

Note. The following designations have been adopted: LRS — laser reactive synthesis; ECR — electron cyclotron resonance; TD — thermal decomposition; DCMRS and DCMNS — direct current magnetron reactive and nonreactive (i.e. sputtering by neutral atoms) sputtering respectively; HFMRS and HFMNS — high-frequency magnetron reactive and nonreactive sputtering respectively.

conclusions concerning the nature of the superstoichiometry of the IP films. Accurate measurements of the X-ray and pycnometric densities as well as detailed elemental and phase analyses are therefore needed. One should bear in mind that the agreement between the results of the determination of the elemental compositions of the films by various methods is not always satisfactory and this problem requires special consideration in almost every case.

Oxygen is one of the commonest impurities in IP. Fig. 4 presents the dependence of the titanium, nitrogen, oxygen, and carbon concentrations on the surfaces of TiN films on the partial pressure of oxygen in a direct current magnetron reactive sputtering (DCMRS) chamber. The plots were constructed from results obtained by the AES method *in situ*.⁷⁹ Analysis demonstrated how important is the 'vacuum hygiene' in the preparation of IP films: at an oxygen partial pressure in excess of $\sim 10^{-6}$ mm Hg (total pressure $\sim 10^{-3}$ mm Hg), a decrease in the nitrogen concentration and an increase in the oxygen impurity content are observed. A similar situation has been noted also for water vapour.

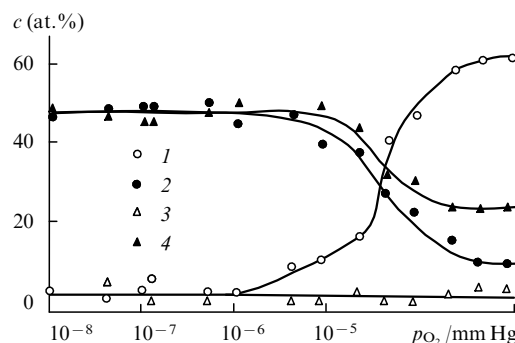


Figure 4. Dependence of the concentrations of oxygen (1), nitrogen (2), carbon (3), and titanium (4) on the surfaces of TiN films on the partial pressure of oxygen.⁷⁹

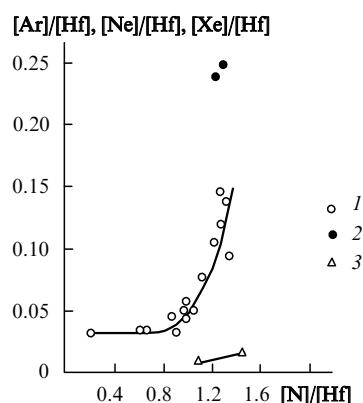


Figure 5. Variation of the contents of argon (1), neon (2), and xenon (3) in the region of homogeneity of hafnium nitride.⁴⁵

The presence in the films of inert gas atoms, entrained in the course of sputtering and implantation, is noteworthy. Fig. 5 presents the dependence of the argon, neon, and xenon contents on the composition of hafnium nitride films synthesised in accordance with the binary ion-stimulated deposition scheme (Fig. 1). The content of the inert gases increases significantly with increase in the amount of nitrogen in the superstoichiometric nitrides, the total amount of these gases being, as expected, inversely proportional to their atomic radius. The above concentration dependence may be associated with increase in the concentration of structural vacancies in the nonstoichiometric phases. An approximately similar situation has been observed also for titanium and zirconium nitrides.

Interesting possibilities of XPS in relation to the analysis of $\text{Ti}(\text{B},\text{N})_x$ films have been demonstrated by Mollart et al.⁸⁰ Fig. 6 presents the XPE spectra of the 1s states of boron and nitrogen in

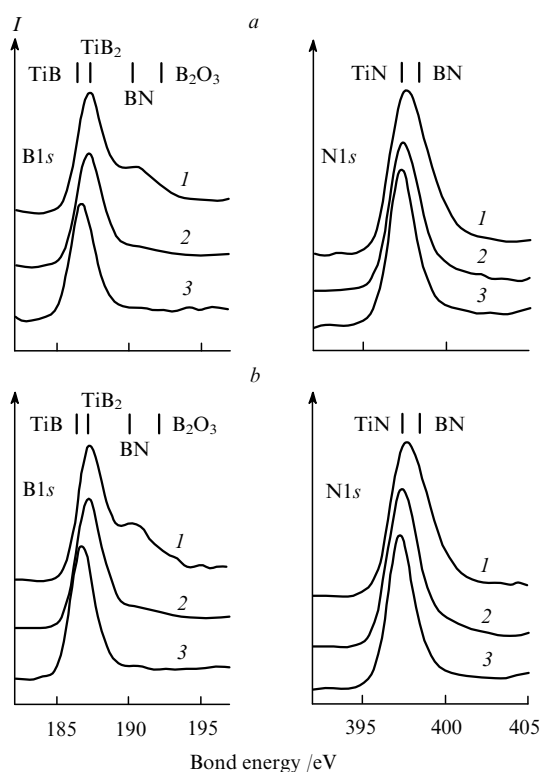


Figure 6. XPE spectra of the 1s states of boron and nitrogen in nitridoboride films of different composition before annealing (a) and after annealing at 400 °C (280 min) (b).⁸⁰ (1) TiB_2N ; (2) $\text{TiBN}_{0.5}$; (3) $\text{Ti}_2\text{BN}_{0.5}$.

nitridoboride films of different composition in the initial and annealed states. The films were obtained by the direct current magnetron nonreactive sputtering (DCMNS) method using $\text{Ti}-\text{BN}$ composite targets of different composition. By employing standards for TiB , TiB_2 , BN , and B_2O_3 , it was possible to estimate with an accuracy of $\pm 30\%$ the phase compositions of different films, which agreed qualitatively with data obtained from the $\text{Ti}-\text{B}-\text{N}$ phase diagram. The XRD and AES methods proved less informative in this respect, although the latter has been recommended for the determination of the $[\text{N}]/[\text{Ti}]$ ratio in titanium nitride.⁸¹

2. Structure and defects

a. Lattice parameters and occupancy of sublattices

The IP structure began to be investigated a long time ago, but an insufficiency of results obtained on well attested objects is nevertheless still felt. It was noted above that accurate measurements of the X-ray and pycnometric densities are needed for the elucidation of the occupancy of the metallic and nonmetallic sublattices in IP. Such densities are nontrivial for low dimensionality objects such as films.

A decrease in the lattice parameter on deviation from stoichiometry has been noted for both the usual⁸² and film^{22,83} titanium nitride specimens (Fig. 7). A similar situation is characteristic also of hafnium nitride.⁸⁴ The absolute values of the lattice parameters for IP films are usually greater than for massive specimens. This is as a rule attributed to the influence of the residual stresses, the grain size, and also the presence of impurities. It is striking that the period depends on the film thickness. A decrease in the lattice parameter with increase in the thickness of TiN , NbN , and CrN films has been noted (it is particularly marked up to a thickness 50–150 nm); on the other hand, for a zirconium nitride film the lattice parameter also increases with increase in thickness.⁸⁵ The presence of an appreciable crystallographic anisotropy in the lattice deformation parameters for the substoichiometric and stoichiometric titanium nitrides is also of interest.⁸³ Thus the relations $a(200) > a(111)$ and $a(200) < a(111)$ are characteristic of $\text{TiN}_{\sim 0.55}$ and $\text{TiN}_{\sim 1.0}$ respectively. The latter relation is also observed for superstoichiometric TiN films, which has been attributed to the possible formation of a phase with a CaF_2 type structure in the form of nanocrystals.⁸⁶ However, an unambiguous treatment of these and other changes in the lattice period in IP films requires additional studies and a detailed elemental analysis.

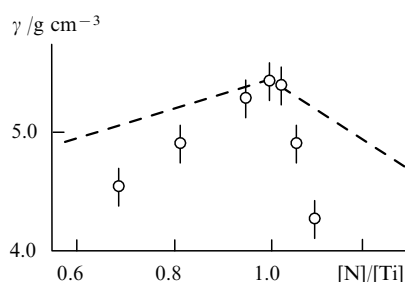


Figure 7. Variation of the density (γ) in the region of homogeneity of titanium nitride films.³²

Dashed line—calculated results obtained, on the basis of a purely vacancy approach.

In a number of investigations, the point defects in the films were studied by positron annihilation spectroscopy.^{84, 87–89} The presence of defects of the type of vacancies, interstitial atoms, micropores, and others has been noted. However, the treatment of the annihilation characteristics in IP with different sublattice occupancy is still far from being fully understood, so that neutron diffraction studies with determination of the locations of light

atoms and of the ordering of structural vacancies might therefore 'throw light' on this problem.

Certain interesting features of the crystal structures of Ti(Si, N, O), NbN, ZrN, LaB₆, CeB₆, SmB₆, ZrB₂, and TiB₂ films (anisotropy of the lattice parameters, the influence of the film thickness on the crystallinity), as well as single crystal film deposition processes, the formation of supersaturated solid solutions, etc. have been examined in a number of investigations.^{77, 90–94} The characteristics of the ordering in IP films remain virtually little investigated, although an appreciable amount of information has accumulated for these compounds in the usual (nonfilm) form.^{2, 10, 20}

b. Residual stresses and texture

The residual stresses in IP and their structure have been thoroughly investigated and described in the literature (see, for example, Refs 22, 24–26, 83, and 95–97). The residual macrostresses are measured by an X-ray method (the so called $\sin^2\psi$ method) and many mechanical methods. It is believed that the residual stresses are due to the difference between the coefficients of linear thermal expansion of the film and the substrate and also to the characteristic features of the film growth. For the majority of PVD films, these stresses are compressive; for TiN CVD films, tensile stresses have been noted.²⁵ Appreciable compressive stresses have been detected also for TiC and TiB₂ PVD films.^{22, 93} It has been observed that the bias voltage and ion bombardment exert a significant influence on the residual stresses.^{26, 83} In the region of homogeneity of TiN, the residual stresses vary nonmonotonically, minimum stresses being characteristic of the TiN_{0.7} composition, to which the maximum hardness corresponds (see below).⁹⁵

The study of the texture of TiN CVD films revealed that the preferred orientations depend on the deposition temperature and on the molar ratio $[\text{TiCl}_4]/[\text{NH}_3](m_{\text{N}}/[\text{Ti}])$.⁹⁸ Three types of preferred orientations have been detected; the $\langle 100 \rangle$ texture is characteristic of low deposition temperatures; the $\langle 110 \rangle$ texture corresponds to moderate temperatures and low values of $m_{\text{N}}/[\text{Ti}]$; the $\langle 111 \rangle$ texture corresponds to high process temperatures and high values of $m_{\text{N}}/[\text{Ti}]$. The changes in the nature of the texture are attributed to the characteristic features of the supersaturation in the gas phase. Weber et al.,⁵² who used the ECR method to activate nitrogen, noted that the preferred $\langle 200 \rangle$ orientation was observed for TiN films when N₂ was employed, while the $\langle 111 \rangle$ texture was characteristic of the film when ammonia was employed. It has also been noted that the latter texture is manifested for titanium nitride (PVD) with a nearly stoichiometric composition (TiN_{0.88–1.0}); for compositions with a lower nitrogen content, the $\langle 311 \rangle$ and $\langle 200 \rangle$ textures predominate.⁹⁵ The influence of substrate layers (titanium nitride or carbide) on the textures of AVID carbide and nitride films respectively and also of multilayer nitride films has been analysed.^{85, 97}

The influence of film thickness and partial nitrogen pressure in PVD processes has been investigated.^{99, 100} With increase in film thickness from 1.3 to 6.8 μm , the preferred texture changed from the $\langle 200 \rangle$ orientation to $\langle 111 \rangle$; the opposite change was observed when the partial nitrogen pressure was increased, which was accompanied by a decrease in the residual compressive stresses. Such changes in texture are associated with the deformations accumulating during the deposition of the films when account is taken of the anisotropy of the surface energies of different crystallographic faces.

Figure 8 illustrates the influence of the thickness of the TiB₂ films obtained by the DCMRS method on the nature of the X-ray peaks.⁹³ The ratio of the intensities of the (001) and (101) reflections is manifested fairly clearly only for thicknesses in excess of 1300 Å. A predominantly random orientation is characteristic of thinner films (Fig. 8a), while the $\langle 001 \rangle$ texture begins to be manifested distinctly when the thickness increases.

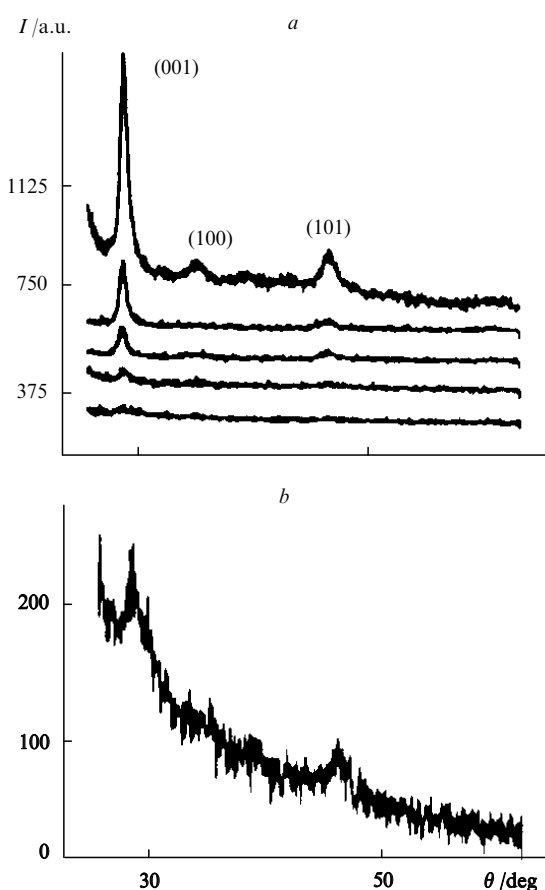


Figure 8. Diffraction patterns for a TiB₂ film obtained at an angle of 5° .⁹³ (a) the influence of thickness; (b) film 860 Å thick; film thickness (Å): (1) 5000; (2) 2800; (3) 1800; (4) 1300; (5) 860.

The thermal stability of texture orientations in IP films has been investigated on a limited scale.

c. Grain size (of crystallites) and morphology

The study of the fine structure [the size of the crystallites (L) and microstrains (ϵ)] and also of the morphology of IP films is needed to elucidate their properties. Fig. 9 presents the (200) and (111) reflections for a titanium nitride film obtained in accordance with the ion-stimulated deposition scheme (Fig. 2).⁴⁶ The broadening of the peaks as the energy of the Xe ions is varied can be seen. The quantity L is estimated from the familiar Scherrer formula using the measured peak width at half-height level. For accurate calculations, it is necessary to take into account the contribution of microdistortions to the width of the peaks. For this purpose, use is made of different modifications of the familiar Warren–Averbach and Williamson–Hall methods.¹⁰¹

Table 3 presents certain results of the determination of the values of L and ϵ for IP films. The size of the crystallites in the films investigated is in most cases < 50 nm and they can therefore be assigned to the class of nanocrystalline (nanostructural) objects. A detailed study of the influence of the temperature of the substrate, the bias voltage, and the duration of sputtering on the value of L estimated from the width of the (111) reflection has been undertaken for TiN.¹⁰⁵ It is of interest that the influence of temperature is manifested distinctly only for a bias voltage of about -60 V, whereas at -100 and -200 V it is virtually absent in the temperature range $150–500^\circ\text{C}$. The influence of various factors on L and ϵ for the magnetron sputtering of a wide variety of targets (TiNi, TiC_{0.5}, TiB + Ti, etc.) has been described.^{78, 107} It was noted in the same investigations, in particular, that the reason for the difference between the values of L determined by the XRD

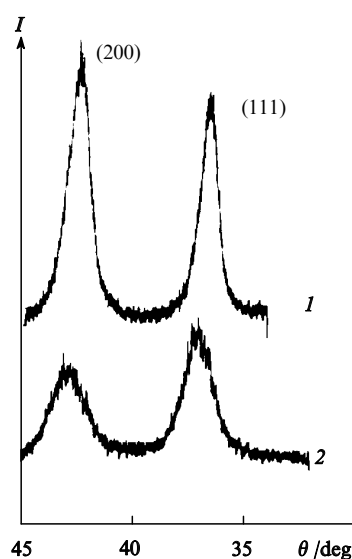


Figure 9. Overall form of the (200) and (111) reflections for a TiN film.⁴⁶ Energy of xenon ions (kV): (1) 40; (2) 20.

Table 3. Dimensions of crystallites and the magnitude of microdistortions.

Compound	Method of preparation	L / nm ^a	$10^3 \varepsilon$	Ref.
TiN _{0.48–1.0}	AVID	9–21	0.8–2.6	95
TiN	IBT	4–8	—	102
Ti ₂ N	"	6–21	—	102
TiN	"	5–20	—	46
TiN	AVID	20	—	103
	DCMRS	35	—	103
TiN	"	23–66	0.8–13	104
TiN	"	30–140	—	105
ZrN	HFMRS	—	9	91
NbC	DCMNS	30–140	—	106

^a The values of L were estimated from the Scherrer formula in addition to the results obtained from the literature.^{91, 95, 104}

and TEM methods may be packing defects, which contribute to the broadening of the X-ray reflections and the block nature of the structure. Such differences for nanocrystalline materials are fairly frequent,¹⁰¹ which is associated with the columnar nature of the morphology of many IP films. A combination of various methods for the determination of L is therefore needed, particularly in relation to multilayer objects.⁹⁶

The presence of edge misfit dislocations with a Burgers vector $1/2 [110]$, characteristic of carbides and nitrides with the NaCl structure, has been detected in multilayer TiN, NbN, VN, and (TiV)N films, which were deposited by the DCMRS method on the (100) face of a MgO single crystal.¹⁰⁸ The relaxation of the stresses with formation of a domain structure under the influence of the differences between the lattice periods and layer thicknesses has been observed. The density of the loop dislocations fell from 5×10^{12} to $1.5 \times 10^{10} \text{ cm}^{-2}$ with increase in the temperature of the single crystal support from 550 to 850 °C, which ensured the formation of single crystal TiN films.¹⁰⁹

The morphology of the structural features of IP films may be characterised as columnar and as random with a wide range of intermediate variants. Fig. 10 presents a typical columnar structure of a TiN film obtained by the DCMRS method.¹¹⁰ In cross section, the size of the crystals reaches 200–300 nm. This photograph clearly illustrates also the presence of a residual plastic deformation of the fibres of the brittle titanium nitride in the

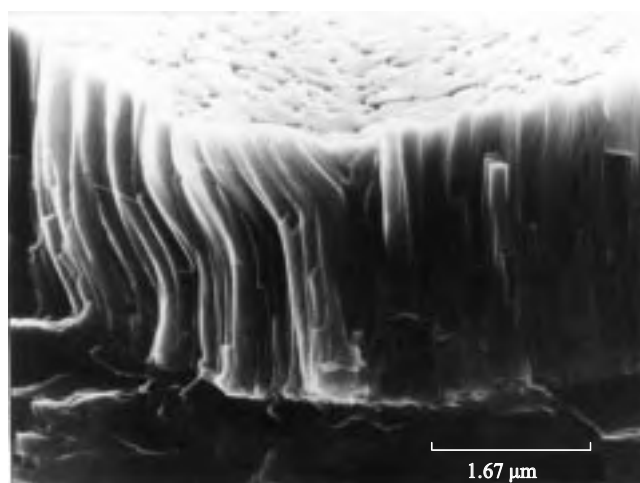


Figure 10. The fracture surface in a TiN film in the region of indentation by the microhardness measuring device.

The photograph was taken on a high-resolution scanning electron microscope (FEG-SEM) and has been kindly provided by Ma and Bloyce.¹¹⁰

region of the microindentation. The influence of the deposition temperature and of the shift potential on the morphology of TiN films has been described.¹⁰⁵ Depending on the deposition conditions, in cross section the form of the crystals varied from triangular to square and their size was between 50 and 500 nm, which is greater by factors of 2–4 respectively than the X-ray determinations of L (Table 3). This difference must be attributed to the approximate nature of the estimates from the Scherrer formula. Another type of fracture in TiN films obtained by the DCMRS method in apparatus with four planar nonbalanced magnetrons (a columnar amorphous structure) has been described by Effoglu et al.¹¹¹ The possibility of obtaining columnar structures by employing stronger magnetic fields was demonstrated in the same study. It is of interest that films with a noncolumnar amorphous structure had more effective mechanical and operational properties. It has also been noted that the imposition of a shift potential during magnetron sputtering promotes the elimination of the porosity of the films.¹¹²

The study of the fractures in boride films (see, for example, Refs 74, 76, 77, 113, and 114) revealed different structural types. A stone-like fracture or a 'cauliflower' type fracture with a partially manifested columnar structure is characteristic of these films, the columnar structure becoming more pronounced with increase in the nitrogen content (Figs 11 and 12). The porosity of the films is usually low or virtually absent, but it must nevertheless be taken into account in the analysis of the properties of the films. The

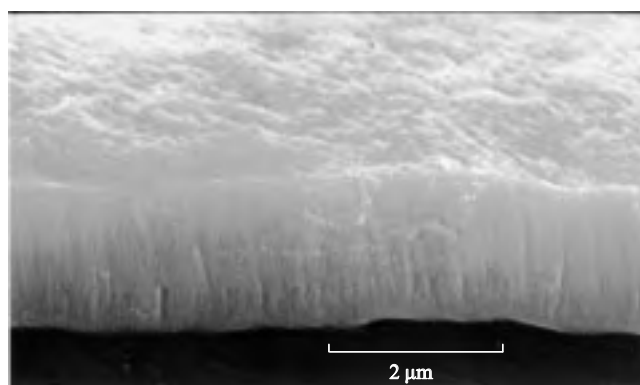


Figure 11. The fracture surface in a TiB₂ film obtained by the DCMNS method.¹¹⁴

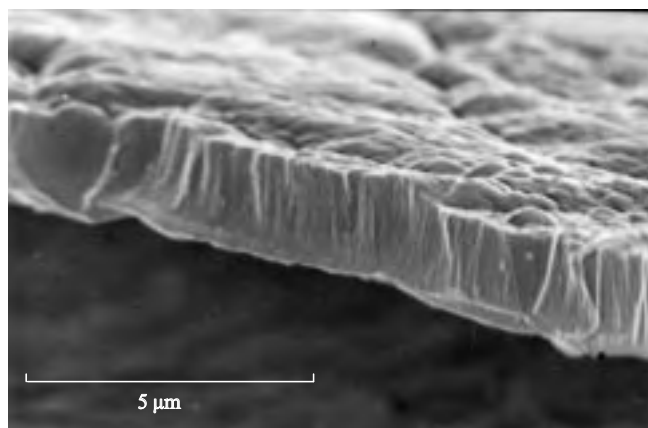


Figure 12. The fracture surface in a Ti(B,N)_x film obtained by the DCMNS method.¹¹⁴

methods for the determination of porosity from electrochemical measurements in relation to TiN, Ti(B, N) , and $(\text{Ti, Al})\text{N}$ films have been described by Aromaa et al.¹¹⁵ and the general features of the macro- and micro-defects in the coatings have been analysed in a monograph.¹¹⁶ We may note that the general level of the porosities of films obtained by the IBT and HFMNS methods was from 0.003% to 0.239%.¹¹⁵ The topography of the film surfaces was investigated both with the aid of scanning electron microscopy (Figs 10–12) and (especially) scanning tunnelling and atomic force microscopy.¹¹⁷

The characteristic features of the morphology of the IP films obtained with the aid of CVD technology have been examined in a series of studies (see, for example, Refs 27, 55, and 118–120). It is important to note that, when two- or three-phase systems (compositions such as TiB_2 – TiC , SiC – TiC – C , TiN – AlN , etc.) are codeposited, nanostructural multilayer and mixed films, coatings, and layers with $L \approx 10$ – 20 nm may be obtained judging from the equilibrium phase diagrams. By virtue of the high process temperatures (~ 1000 – 1100 °C), the rates of deposition are very high (~ 1 mm h^{-1}). For the SiC – TiC – C nanocomposites, a texture in the growth of $(\text{Si, Ti})\text{C}$ crystallites with a transverse dimension of 10–15 nm in the $\langle 220 \rangle$ direction was noted; according to Raman spectroscopic data, the size of the graphite inclusions did not exceed several nanometers.¹¹⁹

Thus a wide spectrum of morphological structures, caused by the diverse influence of the deposition conditions, impurities, and other factors in the PVD and PCD processes, is characteristic of IP films. In a number of studies (see, for example, Refs 24, 26, 121, and 122), attempts were made to put forward schemes which would make it possible to predict the formation of particular structures in the PVD films. The prediction was based on the analysis of homologous deposition temperatures, the gas pressure, the shift potential, etc. Estimates of the conditions for the production of single crystal and polycrystalline formations are available for CVD films.¹²³ However, in the vast majority of cases the predictions are so far qualitative in character.

A schematic illustration of typical morphological structures is presented in Fig. 13 in relation to TiN and $(\text{Ti}_{0.5}\text{Al}_{0.5})\text{N}$ PVD films. The authors of this scheme²⁸ note that, apart from the principal factors indicated (deposition temperatures and ionic characteristics), parameters such as the composition of the plasma-forming gas, the impurities, etc. may greatly alter the nature of the morphology of the deposited films. The wide variety of factors exerting an influence, listed above, does not as yet permit an *a priori* prediction of the formation of particular morphological structures and this question requires further study.

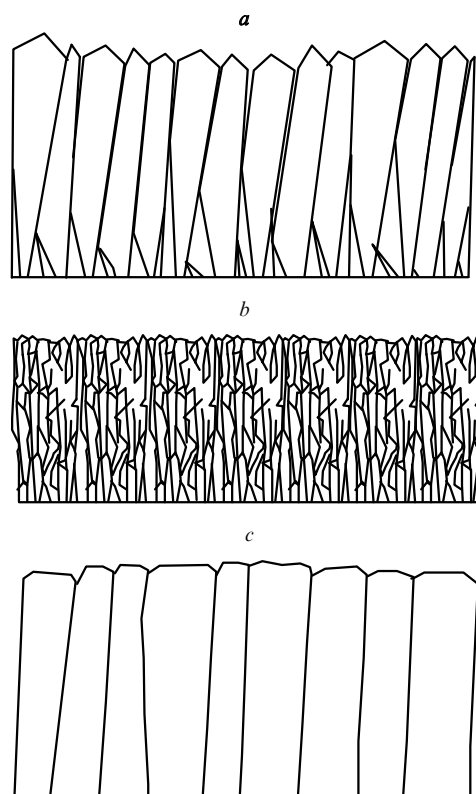


Figure 13. Schematic illustration of typical morphological structures of TiN and $(\text{Ti}_{0.5}\text{Al}_{0.5})\text{N}$ PVD films.²⁸

(a) low deposition temperatures ($T < 500$ °C) and low energy characteristics of the ions; (b) low deposition temperatures and average energy parameters of the ions (100–500 eV) (c) high deposition temperatures ($T > 500$ °C) or low temperatures but high low-energy ion fluxes.

3. Electronic structure and chemical bonding

The electronic structure and chemical bonding in carbide and nitride films have been investigated by numerous workers (see, for example, Refs 21, 55, 56, 84, and 125–128). One of the latest communications devoted to this problem is a review.¹²⁴ The binding energies of Ti $2p_{3/2}$, B $1s$, and N $1s$ core levels have been measured^{80, 125, 127} for Ti(B,N)_x , TiB_2 , and TiN films as well as those of the Ti $2p$, N $1s$, and O $1s$ levels for TiN_x and Ti(N,O)_x films. The effective charges on the titanium, oxygen, and nitrogen atoms have been estimated.¹²⁷ The possible influence of structural defects in IP on the binding energies of the core levels and the difficulties in understanding the nature of the IP have been discussed.⁸⁴ Detailed XPES studies on cubic $(\text{Ti,Al})\text{N}$ films as well as quantum-chemical calculations made it possible to estimate the effective atomic charges and the distribution of the local density of states and to conclude that there is an ionic component in the bonds.^{124, 126} Comparison of the estimated cohesion and substitution energies in titanioaluminium nitrides and carbides showed that the formation of the latter is less probable.

Table 4 presents the experimental binding energies for the $1s$ levels of nitrogen and the levels of the metals in Group IV and V transition metal nitride films synthesised from organometallic precursors and ammonia at low temperatures.^{55, 56} These films were characterised by a low content of impurities (less than 1–2 at.% of oxygen and carbon) and by the small size of the crystallites ($L \approx 2$ – 5 nm). However, the hydrogen content, characterised by the ratio $[\text{H}]/[\text{M}]$, varied in the range 0.5–1.35. The

Table 4. The binding energies (eV), found by the XPS method, for films deposited at 200 °C.^{55, 56}

Compound	Precursor	Energy of N 1s level	Energy level of metal atom	E_M
TiN	Ti(NMe ₂) ₄ /NH ₃	396.9	Ti 2p _{3/2}	454.8
Zr ₃ N ₄	Zr(NMe ₂) ₄ /NH ₃	397.2	Zr 3d _{5/2}	180.3
Hf ₃ N ₄	Hf(NMe ₂) ₄ /NH ₃	397.0	Hf 4f _{7/2}	15.1
VN	V(NMe ₂) ₄ /NH ₃	397.0	V 2p _{3/2}	513.1
Nb ₃ N ₄	Nb(NEt ₂) ₄ /NH ₃	397.4	Nb 3d _{5/2}	204.1
Nb ₃ N ₄	Nb(NMe ₂) ₅ /NH ₃	397.2	Nb 3d _{5/2}	203.9
Ta ₃ N ₅	Ta(NMe ₂) ₅ /NH ₃	396.9	Ta 4f _{7/2}	24.0

binding energies in the films do not differ from those for the nitrides in the usual polycrystalline state^{55, 56} and it has not so far been possible to detect a possible change in the electronic structure in the nanocrystalline state.

IV. Properties

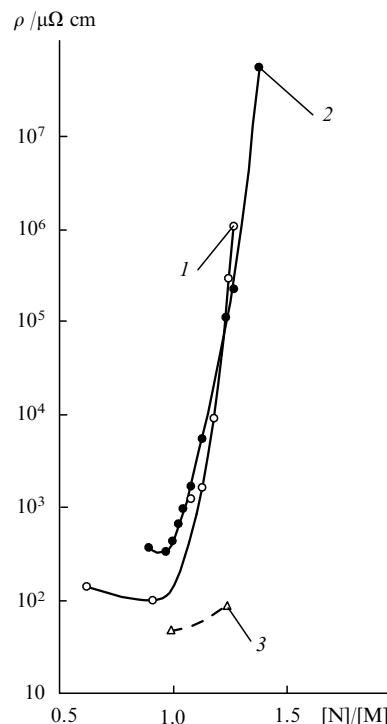
1. Electrical and optical characteristics

a. Electrical resistivity

The metal-like nature of the interstitial phases is manifested primarily in their electrical properties — a low specific resistance (ρ) and a positive coefficient of its temperature dependence ($\alpha = \Delta\rho/\rho\Delta T$). This is associated with the characteristic features of the energy spectrum of the electrons in IP and with the high concentration of carriers.^{2, 7, 17} The level of the resistivity in some of the IP (for example, stoichiometric Group IV transition metal nitrides and borides) is appreciably lower than in the corresponding metals. On the other hand, certain superstoichiometric IP, in particular nitrides, behave as semiconductors and dielectrics. The deviation from stoichiometry has a great influence on the electrical properties. Furthermore, as in the case of metals and alloys, ρ and α are greatly influenced by the overall impurity content and the defectiveness of the structure, including the grain size and the cross-section of the specimens (we have in mind the scattering of the carriers at the grain boundaries and on the outer surfaces). The study of electrical properties is a fairly representative method for the investigation of the composition and ideality of IP films, but a detailed attestation of the test objects is then of course required.

Table 5 presents the results of the determinations of ρ for IP films obtained by different methods. Not all the data are presented, but only those which are most reliable (in this sense the results for TiN are outstanding). In a number of instances, one should not overestimate the value of the information presented, since there are no detailed data on the composition, defectiveness, and thickness of the films. Nevertheless, we shall emphasise certain general characteristics of the results presented in Table 5.

1. The variation of ρ in the region of homogeneity of the IP is not monotonic. This is illustrated in Fig. 14 for TiN, ZrN, and HfN films synthesised in accordance with the ion-stimulated deposition scheme (Fig. 1).⁴⁵ The increase in ρ on deviation from stoichiometry in the decreasing direction ($n < 1$) is usually attributed to the scattering of the carriers by structural vacancies in the nonmetallic sublattice. The considerable increase in ρ for $n > 1$ is due to the transition to compounds with nonmetallic conductivity. A similar situation has been observed for yttrium and lanthanum dihydride and trihydride films.¹⁴⁶ We may also note that, on the one hand, the variation of the electron energy spectra on passing from MN to M₃N₄ has been confirmed also by quantum-chemical calculations¹⁴⁹ and, on the other, the fact that the concentration of inert gases increases in the superstoichiometric nitrides (Fig. 5). At the same time a different type of variation of ρ may be observed in the region of homogeneity, for example, ρ for tungsten nitride films diminishes on deviation from stoichiometry.¹³⁶

**Figure 14.** Variation of the resistivity in the region of homogeneity of HfN (1), ZrN (2), and TiN (3).⁴⁵

2. By comparing the overall level of the values of ρ with the available data for IP (see, for example, Refs 2, 7, and 17), one may note that results indicating a high degree of ideality and a low impurity content have been obtained only in isolated instances (TiN single crystal films¹²⁹ and extremely ideal ZrN films¹³²). This was achieved by employing single crystal supports (MgO and Si) and by the thorough maintenance of other deposition conditions (high temperatures, low ion energies, 'vacuum hygiene', etc.).

Figure 15 presents the dependences of ρ and of the width of the (200) reflection for a ZrN film on the energy of nitrogen ions.¹³² The low values of ρ were determined by the deposition temperature (not above 800 °C) and the corresponding specified generation of nitrogen ions and zirconium atoms ensuring the formation of a zirconium nitride with a nearly stoichiometric composition. The influence on ρ by various conditions in the deposition of TiN films on single crystal silicon supports with a germanium sublayer under the conditions of pulsating laser vaporisation has been analysed in detail.¹³¹

3. It has been noted⁵⁷ that minimal values of ρ have been obtained for a thickness of a TiN CVD film greater than 100–150 nm. For PVD films, the critical thickness was

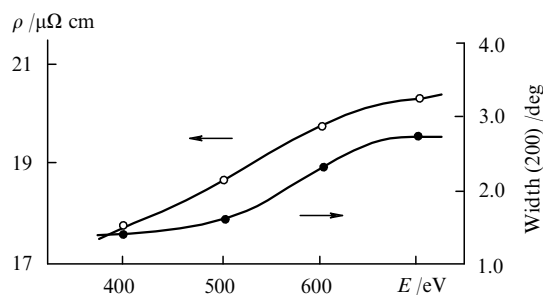
**Figure 15.** Dependence of the resistivity and the width of the (200) reflection for a ZrN film on the energy of nitrogen ions.¹³²

Table 5. The resistivities (ρ) of IP films at room temperature.

Film	Method of preparation	$\rho / \mu\Omega \text{ cm}$	Ref.	Film	Method of preparation	$\rho / \mu\Omega \text{ cm}$	Ref.
Nitrides				Carbides			
Ti ₂ N	DCMRS	~200	22	ZrC _{0.9}	ARV	560	137
Ti(N _{0.72} C _{0.17} O _{0.11}) _{1.38}	ECR	~250	51	NbC _{0.98}	LV	20–50	35
Ti(N _{0.68} C _{0.22} O _{0.10}) _{1.44}	"	~600	51	NbC _{~1.0}	"	4 ($T = 4 \text{ K}$)	138
TiN _{0.86}	"	45	52	Borides			
TiN _{1.02} H _{0.15}	"	100	52	TiB _{~2}	HFMNS	500 (150)	139
TiN _{~1.2}	DCMRS	120	71	TiB _{1–2.1}	DCMNS	~260 (120)	140
TiN _{1.06}	ARV	82	73	TiB _{~2}	"	~150	141
TiN _{0.98}	"	110	73	ZrB _{~2}	"	250 (75)	139
TiN _{~1.0}	DCRMS (single crystal film)	18	129	TiB _{~2}	HFMNS	296	141
TiN _{~1.0}	AVAD (filtered)	20	130	ZrB _{~2}	"	250 (75)	139
TiN _{~1.0}	LV	26	131	Zr(B _{0.67} C _{0.17} O _{0.16}) _{2.25}	TD ($T = 100–270 \text{ }^\circ\text{C}$)	150	60
Zr ₃ N ₄	CVD ($T = 200–400 \text{ }^\circ\text{C}$)	$> 10^6$	55	HfB _x	HFMNS	~370	142
ZrN _{~1.2}	HFMRS	~100	75	HfB _{~2}	"	~230	143
ZrN _{~1.0}	IBT	17.8	132	YB _{~2}	EBE	55	144
Hf ₃ N ₄	CVD ($T = 200–400 \text{ }^\circ\text{C}$)	$> 10^6$	55	YB _{~4}	"	51	144
HfN _x	HRMRS	~200	133	YB _{~6}	"	88	144
VN _x	CVD ($T = 200 \text{ }^\circ\text{C}$)	~10 ³	56	LaB _{~6}	DSMNS	104	144
Nb ₃ N ₄	CVD ($T = 200 \text{ }^\circ\text{C}$)	10 ³ –10 ⁴	56	Hydrides			
NbN _{~1.0}	ECR	75	92	TaH _{0.48}	EBE and hydridation	~46	145
Ta _{~2} N	HFMRS	200	134	YH _{~2.0}	VViH	~50	146
Ta ₃ N ₅	CVD ($T = 200 \text{ }^\circ\text{C}$)	$> 10^6$	56	YH _{~2.85}	"	~10 ⁴	146
MoN _{~1.0}	DCRMS	~480	135	LaH _{~2.0}	"	~40	146
W _{~2} N	"	~400	135	LaH _{~2.85}	"	~10 ⁵	146
Carbides				LaNi ₅ H _x	"	~670	147
TiC _{~1.0}	ARV	40	137	LaCo ₅ H _{~0.5}	"	350–660	148
TiC _{0.8}	CVD	196	137	SmCo ₅ H _x	"	360–440	148

30–40 nm,¹⁵⁰ although the most reliable results were obtained for a thickness of ~260 nm; a preliminary consideration of the role of the scattering of carriers at intergrain boundaries and on the film surfaces has been carried out. These questions appear to have been inadequately investigated for IP films.

4. The results presented for carbide, boride, and hydride films indicate that the optimum conditions for their preparation with an ideal structure have not so far been found. The values of ρ for annealed specimens are indicated in brackets for TiB_{~2} and ZrB_{~2} films, but one should recall that the resistivity ρ of boride single crystals may be an order of magnitude lower (see, for example, Zhurakovskii and Nemchenko¹⁷ and Serebryakova et al.¹⁸).

An important parameter reflecting the influence of purity and ideality and also containing information about the nature of the carriers is the coefficient of the temperature dependence of the resistivity (α). Table 6 presents results reflecting the influence of the conditions in the deposition of TiN films by the HFMRS method on ρ and α and superconducting characteristics. These data clearly indicate the high structural sensitivity of the electrical characteristics. We may note, that according to the results of Johansson et al.,¹²⁹ $\alpha = 6.2 \times 10^{-3} \text{ K}^{-1}$ for ideal single, crystal TiN films ($\rho = 18 \mu\Omega \text{ cm}$) (for a film ~260 nm thick, $\alpha = 6.4 \times 10^{-3} \text{ K}^{-1}$)¹⁵⁰. It has been reported in a review²² that $\alpha = (1–2) \times 10^{-3} \text{ K}^{-1}$ for the majority of the usual TiN films. A negative value of α is characteristic of the nonmetallic type of conductivity, for example, in the case of Zr₃N₄ films.⁷⁶ A different sign of α has been noted for NbN films: positive for single crystal films⁹² and negative for polycrystalline films.¹⁵¹

Table 6. The influence of the conditions in the deposition of TiN on the resistivity (ρ), the temperature coefficient of the resistivity (α), the temperature of the transition to the superconducting state (T_c), and the width of the superconductivity transition (ΔT_c) (film thickness 30–100 nm).¹⁵⁰

Temperature of support/ $^\circ\text{C}$	Bias voltage/V	$\rho / \mu\Omega \text{ cm}$	$10^3 \alpha / \text{K}^{-1}$	T_c / K	$\Delta T_c / \text{K}$
40	0	205–215	0.26	< 4.3	0.04
40	–115	120–135	0.56	< 4.3	0.04
500	0	65–70	1.02	4.84	< 0.02
500	–100	45–60	1.34	5.04	< 0.02

A detailed study of the electrical properties of epitaxial single crystal multilayer TiN–VN films has been undertaken.¹⁵² Measurements of the Hall constant (R_H) and ρ showed that r_H and hence the concentration of carriers $n = 4.5 \times 10^{22} \text{ cm}^{-3}$ is independent of the thickness of the layers, while ρ and the mobility of the carriers (m) increase sharply, like α , with decrease in thickness, starting with 6 nm. For layers more than 10–15 nm thick, the following values were obtained: $\rho \approx 30 \mu\Omega \text{ cm}$, $m \approx 5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and $\alpha \approx 1.6 \times 10^{-1} \text{ K}^{-1}$. Estimation of the free path length (λ) of the electrons within the framework of Drude's model and on the assumption that the Fermi surface is spherical led to $\lambda \approx 4.6 \text{ nm}$ (both for TiN and VN). These estimates are approximate because, for example, the Fermi surface for nitrides is clearly anisotropic. Nevertheless they are probable. The of the electron free path length in TiN (according to the data of Tsai et al.¹⁵⁰) is 39–96 nm (Table 6); according to Krasnovobodtsev et al.,¹³⁸ $\lambda > 40 \text{ nm}$ for stoichiometric NbC films. Unfortunately, the available information about other electrical characteristics (Hall parameters, magnetic resistance, thermo-e.m.f., etc.) for IP

films is limited and is restricted to data for TiN,^{129, 153} HfN,¹³³ and FeTiH.¹⁵⁴

b. Optical properties

Data on the optical properties of IP are important for decorative applications and also for the construction of devices for the direct conversion of energy. It is well known that in the region of homogeneity titanium nitrides have different colours: TiN_{~0.5} is metallic grey, TiN_{~0.8} is bright yellow, TiN_{~0.95–0.97} is golden yellow, and TiN_{1.0} is brown; carbon and oxygen impurities lead to the blackening and the appearance of a blue tint in the specimens. The optical properties of nitride films have been analysed in reviews on the basis of their electronic structures.^{22, 84} The change in optical properties on passing from yttrium dihydride to the trihydride is beautifully illustrated by experiments described by Huiberts et al.¹⁴⁶ and showing that the change in the hydrogen composition of the films is accompanied by a transition from mirror reflection (metal-like $YH_{<2}$) to transparency (nonmetallic $YH_{>2}$) (see also the resistivity ρ in Table 5).

The characteristics of the optical properties of nitride films are presented in Table 7. It is seen that the influence of deviations from stoichiometry is fairly appreciable. The effects associated with the influence of impurities and surface roughness have been analysed.^{55, 156} For ZrN film containing 10 at.% of oxygen, the refractive index proved to be 2.15–2.25.⁵⁵ The optical properties of TiN_xO_y films obtained by the DCMRS method on architectural glass have been analysed by Polato et al.¹⁵⁷ It has been proposed that the stoichiometry of TiN films be monitored *in situ* on the basis of spectroscopic ellipsometric measurements.¹⁵⁸

Table 7. Optical properties of nitride films.

Nitride	Forbidden band width /eV	Refractive index ^a	Reflectance (%) ^b	Ref.
Zr ₃ N ₄	2.2	2.9–3.3		55
Hf ₃ N ₄	2.7	2.4–2.8		55
VN		1.5–1.7		56
Nb ₃ N ₄		1.5–2.7		56
Ta ₃ N ₅	2.7	3.0–3.1		56
TiN _{~1.0}			0.13	57
TiN _{~1.0}			0.20	73
TiN _{0.67}			0.45	73
TiN _{1.04}			0.1	155
TiN _{0.95}			0.15	155
TiN _{0.8}			0.35	155
TiN _{0.52}			0.45	155

^a Determined with the aid of an ellipsometer (wavelength 622.8 nm).

^b Photon energy 2.8 eV.

Boride films are also promising for decorative applications. LaB₆ films have a characteristic violet colour, while ZrB₂ is silver-grey. On doping with nitrogen, the refractive index of the latter remains constant over a wide range of wavelengths and they are extremely corrosion resistant.⁷⁷

2. Hardness

There is no doubt that the measurement of hardness is one of the most popular methods for the investigation of the properties of films, since it is readily accessible and yields much information. However, an unambiguous interpretation of the results obtained by this method is not simple in many instances owing to the high structural sensitivity of hardness and its dependence on the method of measurement and the influence of the load, the film thickness, and the nature of the support. It is difficult to compare the absolute values of hardness and they require a careful analysis. The result of the measurement of the hardness of IP films have

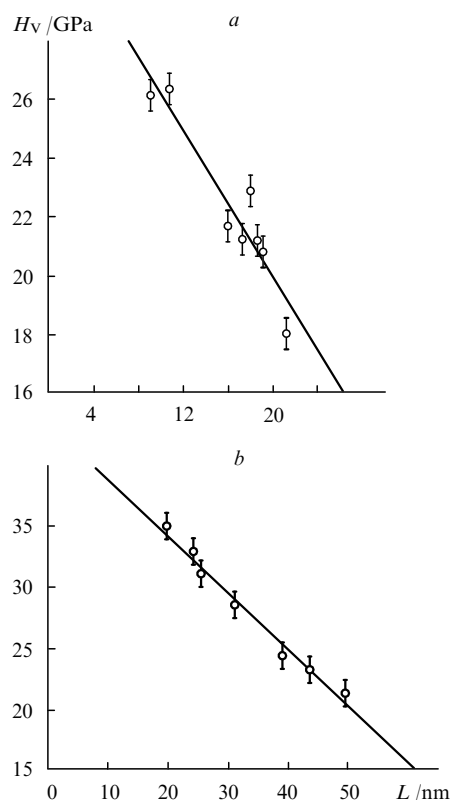


Figure 16. The influence of grain size on hardness.

(a) 1 N load; film thickness 20–25 μm ; support — Ti–6Al–4V alloy;⁹⁵
(b) 0.025 N load; film thickness 1–1.5 μm ; substrate — stainless steel.¹³⁰

been discussed in a number of studies (see, for example, Refs 22–28, 76, 77, 95, 96, 114, 129, 130, and 159–164). We shall consider them for the most thoroughly investigated titanium nitride.

The influence of various factors on the hardness of TiN films is illustrated in Figs 16–18. Much attention has been devoted^{95, 129, 130} to the attestation of the objects of study and the results of these investigations are fully reliable. The familiar Hall–Petch relation, linking hardness (strength) to grain size, holds quite well for films obtained by the AVID method (Fig. 16). Admittedly, it has been noted⁹⁵ that, together with the change in grain size, the nitrogen content and the residual stresses also changed in the films (Fig. 17) and the change was nonmonotonic.

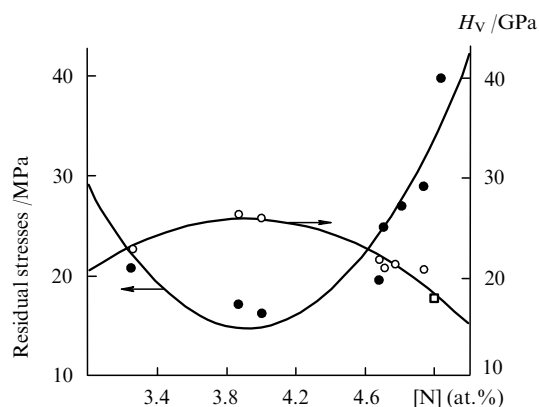


Figure 17. Variation of hardness and residual compressive stresses in the region of homogeneity of TiN.⁹⁵
For conditions, see Fig. 16a.

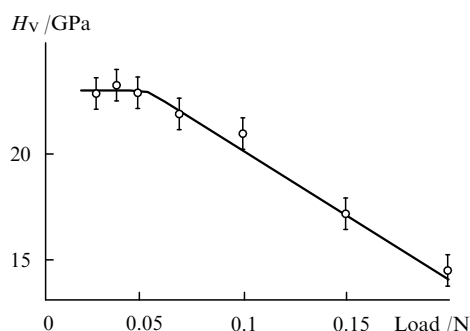


Figure 18. The influence of the load on the hardness of the (111) face of a single-crystal TiN film.¹²⁹ Thickness 2 μm ; substrate — MgO single crystal.

Thus, the relation presented in Fig. 16a reflects the combined influence of such factors on the hardness of the films. The results for the variation of hardness in the region of homogeneity of TiN agree with the latest data published on this question.^{16,82} It is important to stress that the relations presented in Fig. 16 have been obtained for different loads in the tests (the usual Vickers method⁹⁵ and nanoindentation.¹³⁰). The dimensional effect (the influence of the load) is illustrated in Fig. 18, where data for an ideal single crystal TiN film are presented. We may note, however, that certain data of the above studies^{95,130} do not agree with the results of other investigations, (for example, of the influence of residual stresses⁸³). The overall level of film hardness⁹⁵ does not appear very high, which is probably associated with the nature of the support and the thickness of the films in these experiments (in the discussion of the data in Table 3 above, we have already emphasised the uncertainty in the determination of L).

It follows from the foregoing that the treatment of the results of the measurement of hardness is not quite so simple. We endeavoured to collect information about the hardness of IP films and attached to them data on the conditions of preparation and measurement (Table 8). Some of the tabulated results have been estimated by means of the relation proposed by Jonsson and Hogmark.¹⁵⁹ Modelling of the hardness of films on supports as the hardness of composites in many cases leads to entirely reasonable results. The values of Knoop hardness are as a rule lower than those of Vickers hardness. The following comments are useful for a correct interpretation of the data presented in Table 8.

1. The methods and deposition regimes employed exert a considerable influence on the hardness of the films.^{77, 79, 129, 130, 169, 173, 178, 188} The deposition temperature, the shift potential, the characteristics of the ions, the temperature of the subsequent annealing, and other parameters affect the structures of the films and determine their hardness. The results^{178, 188} for TiC–NiB₂ and Ti(B,N)_x films are especially striking in this respect. In the first case, there is a considerable difference between the amorphous and crystalline states (it is not the same for individual compounds and their mixtures). For the boridonitride film, an increase in deposition temperature from 20 to 400 °C also led to an almost twofold increase in hardness. The lower hardness of ZrB₂ and Zr(B,N) films compared with that of titanium diboride and nitridoboride films is also striking. The addition of nitrogen to the former led to the disappearance of the fine columnar structure and the formation of hexagonal boron nitride with a low hardness and effective lubricating properties, which led to an appreciable increase in wear resistance.⁷⁷

2. As a rule, AVID regimes lead to higher hardness parameters compared with other methods. Thus, at the optimum nitrogen pressure and temperature of the support, the hardness of Ti₂N and TiN was respectively ~ 46.5 and ~ 42 GPa (load 0.5 N, film thickness 4–6 μm).^{189, 190} The influence of nitrogen pressure on hardness, lattice period, and half-height peak width of the (111) reflection is illustrated in Fig. 19 for TiN, (TiZr)N, ZrN, and

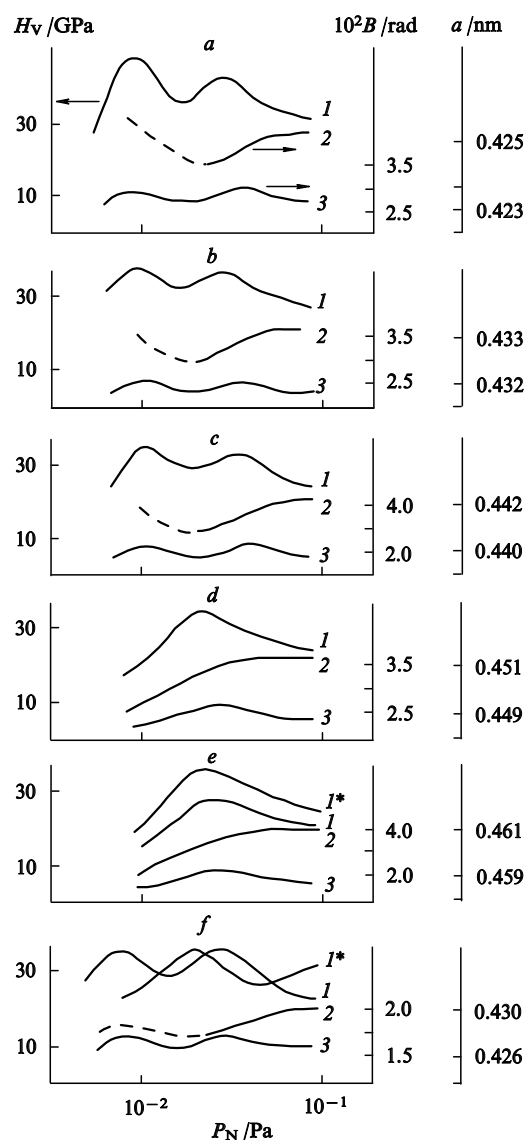


Figure 19. Dependence of hardness (I), lattice parameters (2), and width of the (111) reflection (3) on the nitrogen pressure.¹⁹⁰ (a) TiN; (b) (Ti–25 mass% Zr)N; (c) (Ti–50 mass%, Zr)N; (d) (Ti–75 mass% Zr)N; (e) ZrN; (I^*) (Zr–2 mass% Nb)N; (f) (Ti–21 mass% Mo)N, (I^*) (Ti–31 mass% Mo)N.

(Ti,Mo)N films. It is striking that cubic titanium nitride which has not yet attained the stoichiometric composition has the maximum hardness. The introduction of dopants into TiN (up to 50%) does not alter the general characteristics (Figs 19b and 19c), but films with a higher content of zirconium (Fig. 19d) as well as films of ZrN itself (Fig. 19e) are characterised by a single maximum in the relations presented, because the Zr₂N phase is absent from the Zr–N₂ system. The situation is more complex for (Ti,Mo)N films — in the presence of 21 mass% of Mo it resembles that for weakly doped (Ti,Zr)N films, while a body-centred cubic metallic phase appears for 31 mass% of Mo in the structure and low nitrogen contents.

3. Certain results presented in Table 8 have been obtained in nanoindentation experiments, i.e. for small loads under the conditions of continuous indentation (see, for example, Refs 130, 165, 167, and 168). These data may be somewhat lower than the usual results as a consequence of the influence of the relaxation effect, despite the fact that the influence of the support and of the load is eliminated under nanoindentation conditions (Fig. 18) and this tends to increase the results of the determination

Table 8. Hardness of IP films.

Film	Method of preparation	Thickness / μm	Load / N	Support ^a	Hardness / GPa ^b	Ref.
Nitrides						
TiN _{1.0}	AVID (filtered)	20–25	1	Ti–6Al–4V	17.6±0.9	95
TiN _{0.87}	"	20–25	1	Ti–6Al–4V	21.2±0.5	95
TiN _{0.66}	"	20–25	1	Ti–6Al–4V	25.6±0.8	95
TiN _{0.48}	"	20–25	1	Ti–6Al–4V	22.4±0.9	95
TiN _x	HFMRS	1.8–2.5	0.1	RS	~34.3	110
TiN _x	"	4.8	0.15	RS	(~31.2)	111
(111)TiN~1	DCMRS	2	0.03–0.05	(111)MgO	22.6±0.2	129
TiN~1.0	AVID (filtered)	1–1.5	0.025	SS	34.4	130
TiN _{1.0}	DCMRS	5	0.01–0.03	SS	~24	165
TiN _{0.86}	"	5	0.01–0.03	SS	~28	165
TiN _{0.55}	"	5	0.01–0.03	SS	31–32	165
TiN _{1.53}	IBT	0.3	0.25	SS	~30	166
TiN _{0.9}	"	0.3	0.25	SS	~35	166
TiN _{0.47}	"	0.3	0.25	SS	~27.3	166
TiN _{0.95}	PVD(<i>T</i> = 500 °C)	5	0.025	HA	32.4±3.7	167
ZrN _x	AVID	2–3	0.5	SS	(26–32)	168
ZrN _x	"	2	0.5	HA	27±2	169
HfN _x	"	2–3	0.5	SS	(26–32)	168
(100)VN _x	DCMRS	2.5	0.08	(100)MgO	~15.9±0.2	170
NbN _x	AVID	2	0.5	HA	34±2	169
CrN _x	"	2	0.5	HA	23±2	169
MoN _x	DCMRS	5–20	0.5	SS	35	171
(100)Ti _{0.5} V _{0.5} N _x	"	2.5	0.08	(100)MgO	20±0.3	170
Ti _{0.5} V _{0.5} N _x	AVID	~5	0.5	RS	~32	172
Ti _{0.25} V _{0.75} N _x	"	~5	0.5	RS	~44	172
Ti _{0.5} Al _{0.5} N _x	DCMRS	3	0.1	SS	41±9.8	173
Ti _{0.7} Zr _{0.3} N _x	"	5	0.5	HA	~33	174
(Ti,Al,Zr)N ^c	"	5	0.5	HA	34.3	72
Carbides						
TiC _x	CVD	6.5	0.025	HA	38.9±6.0	167
TiC _x	AVID (700 °C)	5–7	0.5	RS	39.3	175
	(600 °C)	5–7	0.5	RS	36.2	175
TiC~0.85	CVD	15	0.5	HA	~39	176
Ti(C _{0.86} O _{0.14}) _{1.04}	IBT	1.5	0.1	(111)Si	(28.2)	177
TiC _x	DCMNS	5	0.5	HA	33.3	178
TiC _x (amorphous)	"	5	0.5	HA	24.5	178
TaC _x	CVD	8	0.5–3.9	Tantalum	14.6 °	179
MoC _{0.82}	DCMRS	5–20	0.5	SS	30	171
W(C _{0.93} O _{0.07}) _{1.1–1.2}	HFMRS	7	0.01	SS	31	180
WC _x	"	5	0.15	RS	45.5	181
WC _x +Co	"	4.5	0.15	RS	20–39	181
TiC _x N _y	CVD	3	0.025	HA	30.8±3.1	167
TiC _{0.5} N _{0.5}	AVID (600 °C)	5–7	0.5	RS	26	175
TiC _{0.2} N _{0.8}	"	5–7	0.5	RS	25.5	175
Ti _{0.7} Zr _{0.3} C	DCMRS	5	0.5	HA	45	174
Borides						
TiB~2	DCMNS	5	0.5	HA	34	182
TiB~2 (amorphous)	"	5	0.5	HA	23.5	178
TiB~2.8	"	4.1	0.15–0.30	HA	51	183
TiB~2	HFMNS	5	0.25	SS	37.2	184
TiB~1.9	DCMNS	~8	0.5	RS	~62.5	185
TiB~2	IBT	1	0.25–0.75	HA	27.5 °	186
Ti(B,O,N,C) _{2.5} °	DCMNS	1.8	0.5	(100)TiB ₂	44.7±4, 51 °	76
ZrB~2	"	5	0.2	SS	21.6	187
YB _{6.5–7.5}	"	2–5	0.1	SS	17–18	77
LaB _{6.5–7}	"	2–5	0.1	SS	10–29	77
SmB _{6.5–7}	"	2–5	0.1	SS	16–20	77
CeB _{7–7.5}	"	2–5	0.1	SS	15–22	77
TiB _{1.6} N _{0.6}	DCMRS	4.9	0.15–0.30	HA	57	183
TiB _{2.1} N _{0.6}	"	5	0.5	RS	41.5	185

Table 8 (continued).

Film	Method of preparation	Thickness / μm	Load / N	Support ^a	Hardness / GPa ^b	Ref.
Borides						
TiBN _{0.4}	HFMNS					
	20 °C	1–3	(100 nm) ^d	RS	~30	188
	400 °C	1–3	(100 nm) ^d	RS	55	188
TiB _{1.8} C _{0.5}	DCMRS	2.7	0.15–0.30	HA	43	183
TiB ₂ C _{0.4} N _{0.4}	"	4.9	0.1–0.30	HA	50	183
Zr(B,N) _x	"	2–5	0.1	SS	5–20	77

^a Supports: RS — rapidly rusting steel; SS — stainless steel; HA — hard alloy. ^b Vickers hardness; the numerals in brackets represent the Knoop hardness.

^c See also Table 2. ^d Depth of penetration by the indenter. ^e Estimated by the method proposed in the study of Jonsson and Hogmark.¹⁵⁹

of hardness. Yet another characteristic feature of nanoindentation is the possible additional scatter of the results associated with the influence of the roughness of the surface (Figs 10–13)

4. A series of data confirm the Hall–Petch relations as regards films (see Fig. 16 and Miura et al.¹⁹¹), but this problem does not appear to have been exhausted, particularly in view of the need for a detailed structural and other attestation of the films. For example, the nanoindentation of TiN CVD films,¹⁹² deposited on a silicon single crystal at 350 °C, yielded a hardness of 12.7 GPa for a grain size of ~10 nm. This ‘record breaking’ minimal result (see also Gao et al.⁵⁰) requires an explanation. A series of data on WC films^{180, 181} also need interpretation.

5. Alloying is accompanied by an increase in hardness, which has been observed for (Ti,Al)N, (Ti,V)N, (Ti,Nb)N, (Ti,Zr)N, and (Ti,Zr)C films. The presence of oxygen leads as a rule to a decrease in hardness. The influence of nitrogen and carbon atoms is approximately additive. When (Ti,Zr)N and (Ti,Zr)C films are annealed, the spinodal decomposition in the TiN–ZrN and TiC–ZrC systems leads to the formation of a nanocrystalline two-phase structure with a high hardness.^{169, 174} This is clearly seen as regards the influence of the annealing temperature on the hardness of doped and multilayer films based on TiN (Fig. 20). The anomalous behaviour of (Ti,Zr)N films is evident.

These data also demonstrate the advantage of multilayer films compared with monolayer and doped films. Composite or multilayer films (they are also referred to as superlattices) have recently attracted much attention.^{96, 182, 193} Their high hardness and wear-resistance characteristics have been demonstrated in relation to films in a series of systems: TiC–TiB₂, SiC–TiC, B₄C–TiB₂,^{182, 193, 194} TiN–ZrN, TiN–NbN, TiN–CrN,^{85, 169, 195} Ti–VN, TiN–NbN, TiN–(Ti,Nb)N,^{96, 170} TiN–Si₃N₄,¹⁹⁶ and TiN–CN_x.¹⁹⁷ The technological prospects for the combination of CVD and PVD layers have been discussed.¹⁹⁸

Figure 21 illustrates the variation of the hardness of multilayer TiN–ZrN, TiN–NbN, and TiN–CrN films with increase in the number of layers (the overall thickness of all the films was the same and amounted to 2 μm). It is possible to specify at least four factors responsible for the increase in hardness with increase in the number of layers (with decrease in their thickness): the increase in the number of interfaces preventing the propagation of dislocations and cracks; the decrease in grain size in individual layers with decrease in their thickness; the increase in the density of noncorrespondence dislocations and the possible more favourable situation as regards residual stresses in the case of multilayer structures. The nonmonotonic variation of hardness in the case of TiN–CrN films may be attributed to the formation of (Ti,Cr)N solid solution and hence to the disappearance of interfaces, which has been confirmed by X-ray phase studies. The formation of a limited amount of solid solutions has also been detected for TiN–NbN and TiN–ZrN films even for the maximum number of layers (180) and individual nitrides continued to be detected by the XRD method. This confirms the major role of interfaces. The reasons for the high hardness of multilayer films have also been

discussed in reviews.^{28, 96} Attention has been turned to the appreciable difference between the elastic properties of the layers in superlattices.

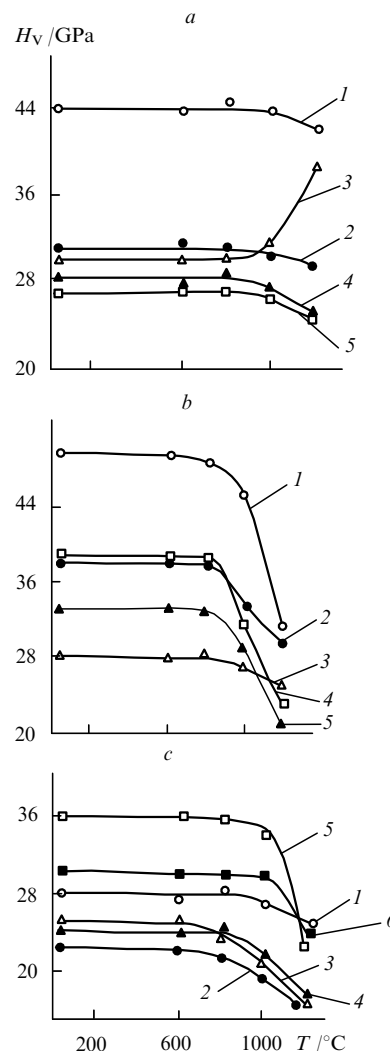


Figure 20. The influence of annealing temperature on the hardness of monolayer (TiN, ZrN, NbN, CrN, Cr₂N), multilayer (TiN–ZrN, TiN–NbN, TiN–CrN), and alloyed [(Ti, Zr)N, (Ti,Nb)N, and (Ti,Cr)N] films.¹⁶⁹

a: (1) TiN–ZrN, 20 layers; (2) TiN–ZrN, 10 layers; (3) (Ti,Zr)N; (4) TiN; (5) ZrN; *b:* (1) TiN–NbN, 20 layers; (2) TiN–NbN, 10 layers; (3) TiN; (4) NbN; (5) (Ti,Nb)N; *c:* (1) TiN; (2) CrN; (3) Cr₂N; (4) (Ti,Cr)N; (5) TiN–CrN, 20 layers; (6) TiN–CrN, 10 layers.

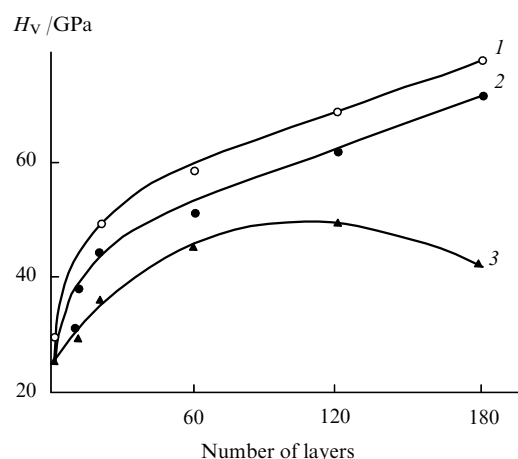


Figure 21. Dependence of the hardness of multilayer nitride films on the number of layers.⁸⁵
(1) TiN–NbN; (2) TiN–ZrN; (3) TiN–CrN.

It is of interest that after some time (possibly several months, which could not unfortunately be established) the high hardness of the TiN–NbN and TiN–ZrN films vanished, evidently as a consequence of the diffusional dissipation of the individual layers.⁸⁵ The existence of relaxation effects in multilayer nitride films has also been noted by Hultman et al.¹⁰⁸ The problem of the stability of multilayer structures over a wide temperature range requires separate study.

The short-term high-temperature hardness of TiN, HfN, ZrN, (Ti,Al)N, and TiC–TiB₂ films has been investigated at temperatures up to 1000 °C.^{178, 199} Whereas the hardnesses of nitride films differ insignificantly up to 1000 °C (8–10 GPa), the difference for TiC, TiB₂, and TiC–TiB₂ films is more significant (for example, at 900 °C it amounts to ~20 GPa for NiB₂–20% TiC and ~9 GPa for TiB₂–50% TiC). It may be that this situation is due to the manifestation of high-temperature superplasticity in two-phase equimolar mixtures, which was observed in experiments on creep for these and other two-phase compositions based on refractory compounds (see, for example, Refs 16, 32, and 33).

It must be emphasised that the knowledge of hardness is useful for correlation with numerous properties important in the practical employment of the films. Such characteristics are determined in tests of the specimens for wear resistance, for microscratching in the study of the adhesion of the films and coatings, and for microbrittleness and cracking resistance in the modelling of disintegration under a concentrated load, etc. (see, for example, Refs 16, 24, 25, 200, and 201). However, these processes will not be considered here.

3. Other characteristics

Table 9 presents data on the elastic properties. In the analysis of these results, one should bear in mind that the absolute values of the elastic properties are influenced not only by the method of preparation, which determines the structure, texture, composition, and size of the specimens, but also by the method of measurement (see, for example, the relevant reviews^{164, 165}). For stoichiometric TiN and ZrN, the results of Torok et al.²⁰² are the most representative. They agree well with the results of the study of Portnoi et al.²⁰⁸ obtained on analogous nonporous nitride

Table 9. The normal moduli of elasticity (E), moduli of shear (G), and Poisson coefficients (ν) for IP films.

Film	Method of preparation	Method of measurement ^a	Thickness / μm	Texture	E / GPa	G / GPa	ν	Ref.
Nitrides								
TiN _{1.0}	DCMRS	1	4–6	< 220 >	637	—	—	202
TiN _{0.5–1.0}	"	2	5	—	300–450	—	—	165
TiN _x	"	3	5	< 311 >, < 200 >	—	—	0.30	203
TiN _{0.97}	"	2	0.2–1	< 111 >	550±50	—	—	204
TiN _{~0.8}	IBT	2	0.3–0.9	—	~450	—	—	205
TiN _{~0.8}	"	4	0.3–0.9	—	—	~130	—	205
TiN _{0.8}	HFMRS	2	1–3	—	410	—	—	188
TiN _x	DCMRS	4	2	—	—	~192	—	206
TiN _x	AVID	2	2	—	370±81	—	—	207
ZrN _{~1.0}	DCMRS	1	4–6	< 111 >	460	—	—	202
ZrN _x	"	3	5	< 200 >, < 111 >	—	—	0.19	203
HfN _{~1.0}	"	1	4–6	< 311 >	380	—	—	202
HfN _x	"	3	5	< 311 >, < 111 >	—	—	0.35	203
VN _x	"	4	2	—	—	~149	—	206
NbN _x	"	4	2	—	—	~142	—	206
(V,Nb)N _x	"	4	2	—	—	~124	—	206
(Ti,Al)N _x	AVID	2	2	—	298±72	—	—	207
(Ti,Nb)N _x	"	2	2	—	375±43	—	—	207
Carbides								
TiC _{~1.0}	DCMRS	1	4–6	< 111 >	460	—	—	202
Ti(C,N) _x	AVID	2	2	—	300±30	—	—	207
Borides								
TiB ₂ N _{0.6}	HFMNS	2	1–3	—	640	—	—	188
TiB _{1.4} N _{0.5}	"	2	1–3	—	750	—	—	188
TiBN _{0.4}	"	2	1–3	—	500	—	—	188
TiB _{0.7} N _{0.5}	"	2	1–3	—	453	—	—	188
TiB _{0.6} N _{0.5}	"	2	1–3	—	276	—	—	188

^a Methods of measurement: (1) resonance bending vibrations; (2) nanoindentation (3) X-ray studies; (4) Brillouin scattering.

specimens prepared by the method involving, the through-saturation of the metals with nitrogen.

The nanoindentation method, involving the analysis of the form of the load-release curve, has come to be widely used in the study of elastic properties (as in the study of hardness). However, not all the results obtained by this method (for example, the data of Vancoille et al.²⁰⁷) have been reasonably interpreted. The high values of the modules of elasticity (E) for certain boridonitride films are also noteworthy.¹⁸⁸ It is likewise of interest that the decrease in the deposition temperature from 400 to 20 °C led to a decrease in E by a factor of almost 1.5 (TiBN_{0.5}). It has been noted²⁰⁷ that annealing of the films leads to an increase in their modulus of elasticity, but above 500 °C it diminishes. In the study of multilayer films, anomalies in elastic properties were not observed for the TiN–(V,Nb)N system, in contrast to hardness.²⁰⁹

The tribological and corrosion properties of IP films^{24, 25, 77, 111, 113, 115, 198, 210–215} have been the subject of numerous investigations. At the same time, problems such as those of phase equilibria and the thermodynamic, thermal, and diffusion properties have been studied to an extremely limited extent in relation to IP films.^{32, 33, 216} So far as we are aware, the available information about diffusion is limited to studies on films as barrier layers (see, for example, Ostling et al.²¹⁷ and Shin et al.²¹⁸). The thermodynamic properties and phase equilibria have been investigated for certain hydride films [VH(D)_x and PdH_x].^{219, 220} In particular, a change in the nature of the isotherms and a decrease in the critical point for decomposition have been noted in the palladium–hydrogen system for films ~50 nm thick as a possible result of the influence of nanocrystallinity on the equilibrium in this system (for films 300 nm thick, anomalies were not observed).²²⁰ On the other hand, for vanadium films 500 nm thick and with a grain size of ~50 nm, measurements of the partial and integral thermodynamic properties revealed no differences relative to the usual polycrystalline vanadium on interaction with hydrogen.²¹⁹ The emission characteristics of lanthanide boride films are discussed in a review.⁷⁷

The thermal stabilities and the recrystallisation of IP films have been studied by a series of investigators (see, for example, Refs 93, 169, 174, 195, 199, 207, and 221–223). It is well known that the formation of a granular structure and recrystallisation begin even during the deposition of the films. Fig. 22 illustrates the influence of film thickness on the grain size for various nitrides. There is an evident difference between ZrN, on the one hand, and TiN, NbN, and CrN, on the other. It may be that this is associated with the greater affinity of zirconium for nitrogen and

Table 10. The grain sizes in nitride films 2 µm thick obtained by the AVID method.²²³

Film	Grain size/µm			Energy of mixing in (Ti, M)N system /kJ mol ⁻¹
	I	II	III	
TiN	0.18±0.08			
CrN	0.16±0.08	0.17±0.05	0.18±0.04	3.4
NbN	0.14±0.03	0.04±0.01	0.08±0.02	6.1
ZrN	0.03±0.02	~0.01	0.02±0.01	32.6
AlN	0.15±0.05	0.08±0.03	~0.01	37.2

Note. The following designations have been adopted: (I) unalloyed film; (II) multilayer TiN–MN film (10–20 layers); alloyed (Ti,M)N film.

the higher energy of zirconium ions. It is of interest that the smallest grains are observed also in multilayer and doped films with ZrN (Table 10). This is also correlated with the high energy of mixing in the TiN–ZrN system. The latter characteristic is known to be related to the diffusional and recrystallisation mobilities.

The influence of film thickness, alloying, and multilayer structure on the recrystallisation of a series of nitrides has been investigated in a number of studies.^{169, 195, 221, 223} Fig. 23 illustrates this in relation to TiN and NbN. The recrystallisation of TiN and NbN begins at virtually identical temperatures, although a greater spread in size is characteristic of TiN. It is also evident that thinner films recrystallise more intensely, but in multilayer and doped structures this process is retarded, especially in the case of TiN–ZrN and (Ti,Zr)N (Table 10). Many details and the mechanism of the high-temperature behaviour of IP films require additional studies.

V. Conclusion

The available information about IP films is diverse but inhomogeneous. Most of it refers to nitrides and, in particular, to TiN. Much less is known about carbides and hydrides, borides occupying an intermediate position. However, so far as one can judge from the problems dealt with in the latest symposia on borides (Austria, August, 1996) and hydrides (Switzerland, August, 1996), there is a growing interest in boride and hydride films. The reactivity and catalytic properties of thin carbide and nitride layers are also being comprehensively investigated.²²⁴ In the present review, the author, whilst not claiming to examine all the problems of film IP, has endeavoured to emphasise certain unsolved problems and in this connection the available information about the structures and physicochemical properties of these objects appears far from complete. For example, the data on the structures of the interfaces for IP films are greatly inferior to those for metals.²²⁵ It is thought that the accumulation of new fundamental results for IP films will promote the development of the physicochemical foundations of the nanostructural materials science and the expansion of the range of their diverse applications.

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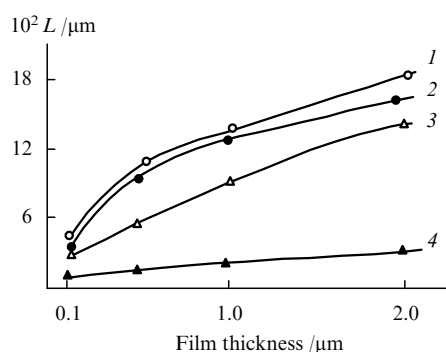


Figure 22. Dependence of grain size on the thickness of the films.²²³ (1) TiN; (2) CrN; (3) NbN; (4) ZrN.

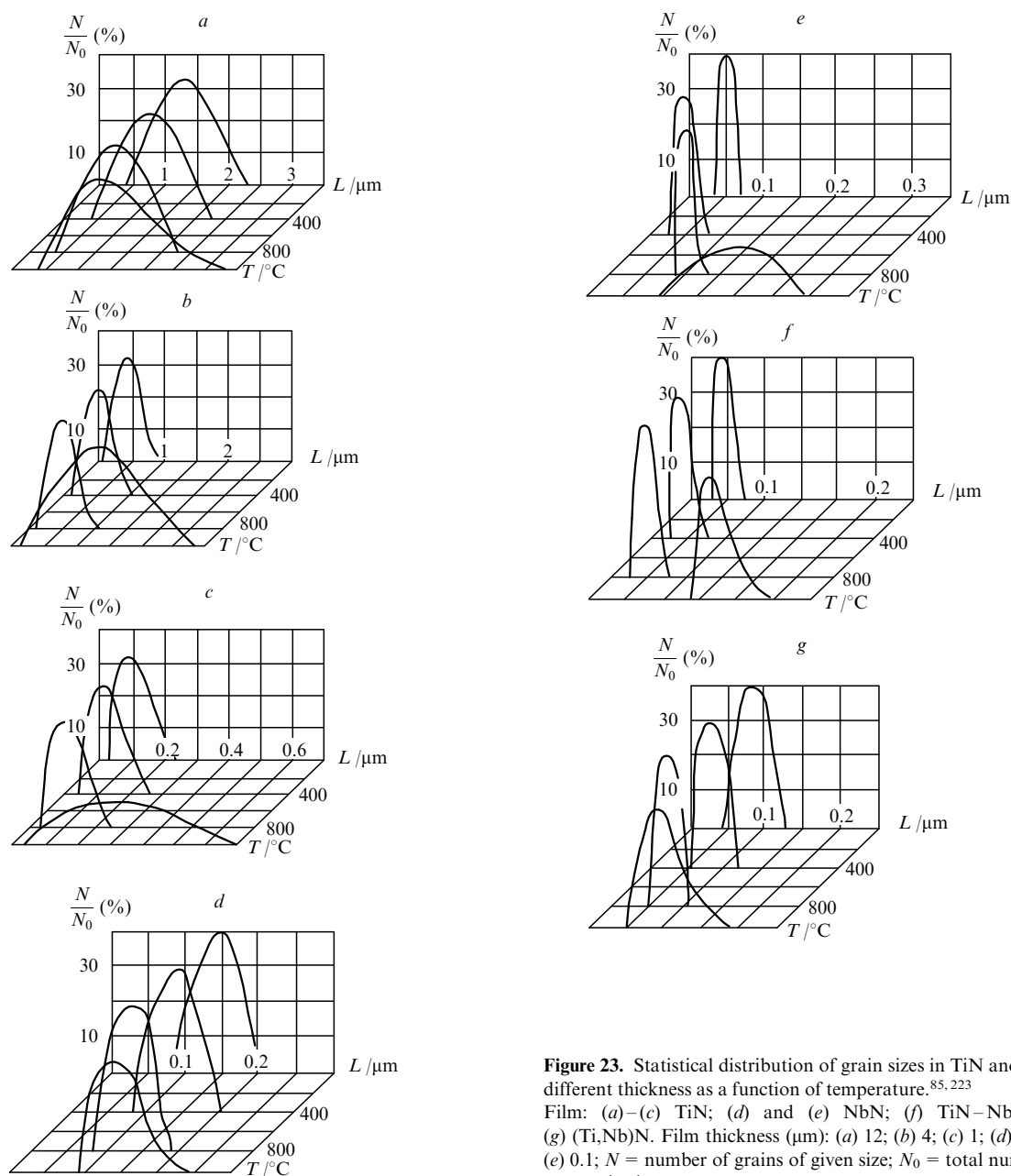


Figure 23. Statistical distribution of grain sizes in TiN and NbN films of different thickness as a function of temperature.^{85, 223} Film: (a)–(c) TiN; (d) and (e) NbN; (f) TiN–NbN, 20 layers; (g) (Ti,Nb)N. Film thickness (μm): (a) 12; (b) 4; (c) 1; (d), (f), and (g) 2; (e) 0.1; N = number of grains of given size; N_0 = total number of grains; L = grain size.

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Labile products of interaction of cellulose with nitrogen oxide compounds

E V Gert

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Abstract. Data concerning the conditions and kinetics of the formation, the methods for identification and isolation, the chemical and physical properties, and the crystal structure of cellulose trinitrate are presented. The conditions governing the formation of Knecht' sorption compound and other unstable crystalline products in the cellulose–N₂O₄ system are also discussed. The primary role of labile derivatives in the manifestation of polymorphism by cellulose on its regeneration from these compounds is demonstrated. The causes of the amorphisation of cellulose, which may occur in these systems, are examined. Examples of a rational combination of several functions of the reaction medium and of the labile nitrogen-containing compound present in it in the preparation of other materials of practical importance from polysaccharides (sulfate and acetate esters and structurally and chemically modified powdered forms of cellulose) are presented. The bibliography includes 160 references.

I. Introduction

The possibilities for the chemical and physical transformation of cellulose (Cel) with the aid of nitrogen oxide compounds (N₂O₄, NO₂, N₂O₃, HNO₃) are extremely diverse. The use of these compounds in oxidation,^{1,2} nitration,^{3,4} degradation,^{5,6} bleaching,^{7,8} and structural modification^{9–12} of cellulose, the dissolution of cellulose in aprotic electron-donating organic media,^{13–15} and its conversion into various derivatives,^{16–18} fibres,^{13,19–21} membranes,^{22–24} and composite materials^{20,25} is well known. In terms of the 'universality index', nitrogen oxide compounds (in the first place N₂O₄) are superior to all known reagents which actively interact with cellulose. The nature of the transformations of cellulose on treatment with these compounds depends on the reaction conditions.

The postulated formation in the given systems of labile cellulose derivatives and their influence on the course of the transformations and the properties of the final products have long been the subject of controversy. A key chemical compound of this type is cellulose nitrite. The decrease in the stability of pyroxylin has been attributed to its presence.^{3,26} The familiar

mechanism²⁸ of the oxidation of cellulose to monocarboxycellulose, where the role of an intermediate was assigned to cellulose nitrite, has been supported² and rejected.^{1,27} The dissolution of cellulose in aprotic organic media containing N₂O₄ is to this day explained in different ways. Some investigators^{13,16–18} postulate the formation of cellulose nitrite whilst others¹⁵ believe that molecular complexes are formed. The absence of information about cellulose nitrite as an individual compound as well as the lack of reliable methods for its detection in a complex reaction medium gave to this cellulose derivative the attributes of a 'hypothetical compound' until recently.

An unstable sorption product characteristic of the given systems is the adduct of cellulose with HNO₃, the existence of which was established at the beginning of this century by Knecht²⁹ and was subsequently called Knecht's compound (KC).^{30,31} It has been suggested that the formation of KC precedes the nitration of cellulose.³ For many decades KC remained 'in the shade' and neither its chemical composition and structure nor its crystal structure have been established hitherto. Nevertheless, communications have recently appeared,^{32,34} indicating the possibility of an effective practical application of KC.

Cellulose nitrite and molecular complexes as possible alternatives to the latter have been considered in reviews^{13–15} merely in the context of their probable participation in the dissolution of cellulose. Their formation was postulated on the basis of a series of indirect experimental pieces of evidence. It was not until the 1980s that the labile products of the interaction of cellulose with N₂O₄ became the object of special comprehensive investigations and fairly extensive experimental data have now accumulated in this field. The high degree of stoichiometry of the interaction observed in this system has led to the possibility of the effective employment of X-ray diffraction for the detection of cellulose nitrite, KC, and other unstable compounds in terms of their crystalline phases in a complex reaction mixture. The primary role of labile derivatives of cellulose also in the observed diversity of the heterophase structural transformations of cellulose, which do not lead ultimately to an alteration of its chemical composition, has been elucidated. The application of new methods made it possible to overcome the 'inaccessibility' of cellulose trinitrate.

Data concerning the conditions and kinetics of the formation, the methods for the identification and isolation, the crystal structure, the properties, and the applied importance of labile nitrogen-containing derivatives of cellulose compounds should be of interest to a wide range of specialists in the field of the chemistry and physics of cellulose. The present review is the first attempt at a systematic account and survey of this scattered information.

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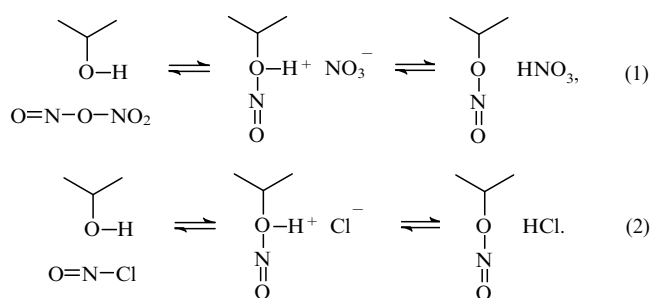
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II. Analysis of ideas concerning the preparation and isolation of cellulose nitrite

The first mention of cellulose nitrite is in the communication of Nicolardot and Chertier.³⁵ Its authors detected nitrite ester groups in the product of the interaction of cellulose with a mixture of nitrogen oxides and acetic acid (AA). The formation of cellulose nitrite was postulated in the nitration of cellulose by compositions containing nitrogen oxides in connection with the search for ways of increasing the stability of nitrocellulose.²⁶

Studies on the formation reaction of monocarboxycellulose have shown that the UV and visible spectra of cellulose treated with gaseous nitrogen oxides exhibit a series of absorption bands at 350, 341.5, 355, and 365 nm, which may be due either to HNO_2 or to cellulose nitrite. A detailed experimental test of both possibilities indicated that these bands are due to the cellulose nitrite spectrum.²⁸ A mechanism postulating that the oxidation of cellulose by nitrogen oxides proceeds via the formation of cellulose nitrite as an intermediate has been put forward.

The practical importance of cellulose nitrite was revealed by numerous studies^{13–18, 36–53} concerning the use of nitrosyl-containing compounds — N_2O_4 , NOCl , $\text{NO}[\text{SO}_4\text{H}]$, etc. — in combination with aprotic organic solvents for the dissolution of cellulose. Fowler et al.³⁶ observed that in nonpolar solvents N_2O_4 has a strong oxidising effect on cellulose, whereas in polar solvents increased swelling takes place or the polymer dissolves without appreciable oxidation. The most suitable organic components from the standpoint of the preparation and processing of the solutions proved to be dimethylformamide (DMF), dimethyl sulfoxide (DMSO), dimethylacetamide (DMA), and ethyl acetate (EA).^{15, 27} The formation of the nitrosyl nitrate form of N_2O_4 ($\text{NO}^+ \text{NO}_3^-$) in polar solvents in the presence of this isomer even in HNO_3 -free liquid N_2O_4 has been demonstrated^{54–56} the interaction of the strong electron acceptor NO^+ with the oxygen atom of the hydroxy-group of cellulose, which functions as an electron donor, is typical for these systems.^{16, 42, 44, 46} Such interaction leads to the formation of cellulose nitrite and HNO_3 , which dissolve in the reaction medium. The organic solvent binds HNO_3 , displacing thereby the equilibrium towards the formation of cellulose nitrite. Total dissolution is ensured for the molar ratio N_2O_4 :Cel = 3. When NOCl is combined with DMF, the ratio is 8.^{13, 16} In contrast to N_2O_4 , nitrosyl chloride itself interacts chemically with DMF.¹⁵ The following mechanism of the electrophilic substitution involving all the hydroxy-groups of cellulose has been proposed:¹⁶



This view is also adhered to by Ermolenko,²⁸ who postulated the formation of cellulose nitrite from its adsorption compound with the nitrosyl nitrate form of N_2O_4 .

The high sensitivity of solutions of cellulose nitrite in nitrosating compositions to water and alcohols has been noted.^{38, 39, 44–47} The regeneration of cellulose is catalyzed by the acid present in the system, which corresponds to the inversion of reactions (1) and (2). The chemical composition of the substance isolated on hydrolysis or alcoholysis hardly differs from that of the initial cellulose.^{13, 16, 44, 46} The acid present in the solution induces the depolymerisation of the macromolecules when the solution is maintained at room temperature.¹⁶ Allowing the solutions to stand in the cold (5 °C) for between 6 h and 12 days does not reduce appreciably the degree of polymerisation (DP) of

the cellulose regenerated from them. Depolymerisation occurs also during the nitrosation process.^{52, 53} The degree of depolymerisation depends greatly on the moisture content of cellulose stirring of the solutions promotes depolymerisation.⁵²

The possibility of synthesising in solution other uniformly substituted cellulose derivatives has been attributed to the formation of cellulose nitrite and to its reactivity in transesterification reactions.^{16–18, 41 43, 50} The water-soluble cellulose nitrate has been obtained by Schweiger¹⁶ as a result of heating a solution of cellulose nitrite in the N_2O_4 –DMF mixture for 70 min at 90 °C. Its degree of substitution (DS) was only 0.5. The HNO_3 accumulated in the system as a result of the nitrosation of cellulose proved to be sufficient for the reaction to occur. These results explained the observations of Clermont and coworkers,^{41–43} who carried out similar experiments and who postulated that the weakly substituted highly degraded product formed is a mixed cellulose nitrite–nitrate. At room temperature, cellulose is not nitrated in the given system. Even after the solution has been kept together with added HNO_3 for 20 h (molar ratio HNO_3 :Cel = 9), only traces of nitro-groups are detected in the precipitated product (DS = 0.04).⁴⁷

Low-molecular-mass alkyl nitrites, including those obtained by treating monohydroxylic alcohols with N_2O_4 , can be isolated after diluting the reaction medium with water, in which they are insoluble.^{44, 57} Polyol nitrites are much less stable than the nitrites of monohydroxylic alcohols,⁵⁸ which can be accounted for by the anchimeric facilitation of the hydrolytic reaction by the vicinal nitrite ester groups. For example, the nitrites of poly(vinyl alcohol) and glycerol cannot be isolated on dilution with water owing to their low hydrolytic stability in acid media. The stability of cellulose nitrite is even lower because of the extensive capillary-porous system of the fibre, which increases the area of the reactive surface. Schweiger^{16, 44} precipitated cellulose nitrite with ice water from a solution to which a strong organic base (pyridine, quinoline, or triethylamine) had been added. The role of the base consisted in inhibiting the acid catalysis of the elimination of the nitrite ester groups. The white deposit isolated was washed with ice water, hydrolysed in an acid medium, and the HNO_2 content in the liquid over the precipitated polymer was determined. The moist cellulose nitrite thus obtained may be stored for a long time in the cold without decomposition. All attempts to dry it led to decomposition. Wagenknecht and coworkers^{46, 48} precipitated and analysed cellulose nitrite in accordance with the same scheme, employing a mixture of diethyl ether (DE) and methylene chloride as the precipitant. The nitrogen content in the precipitates corresponded to a degree of substitution of 2.50–2.95 in terms of the nitrite ester groups,⁴⁶ which, together with the ease of their hydrolysis or alcoholysis, indicated the occurrence of *O*-nitrosation.

The product isolated by Schweiger^{16, 44} was identified more rigorously by Torgashov et al.⁵⁹ Analysis of the deposit for nitrogen in the nitrate and nitrite forms demonstrated that the latter predominated greatly (2.85 against 0.01 in terms of the degree of substitution). For the first time, the IR and UV spectra of a preparation of an individual highly substituted cellulose nitrite were presented. The nitrite was prepared by the following method. The fibrous deposit from which excess water had been squeezed out was dissolved in ethyl acetate cooled to 5 °C. Water was removed from the resulting solution by successive freezing and treatment with calcium chloride. Specimen films for spectroscopic study were cast on KRS-5 or quartz plates in a vacuum desiccator over P_2O_5 . The IR spectrum of such a film (Fig. 1) hardly exhibits the band due to the stretching vibrations of the cellulose OH groups (3100–3500 cm^{-1}) as a consequence of the high degree of substitution, which is 2.85. The two new intense bands at 780 and 1680 cm^{-1} correspond to the stretching vibrations of the O–N and N=O bonds in organic nitrites.⁶⁰ The low-intensity bands at 510 and 650 cm^{-1} may be assigned to the deformation vibrations of the O=N–O group.

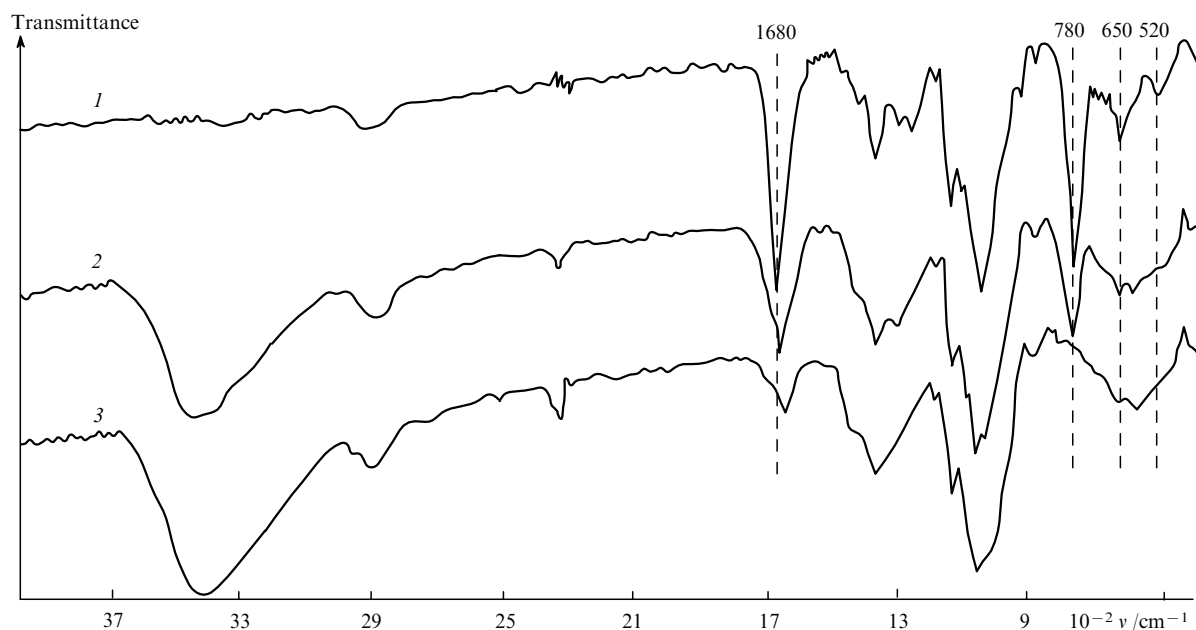


Figure 1. IR spectra of the initial cellulose nitrite film (1) after keeping in air for 30 min (2), and after 2 min contact with ethanol (3).

An obligatory condition for the measurement of such a spectrum is the reduction to a minimum of the contact between the specimen and the moisture in the ambient medium during all the preparatory operations. In air with a relative humidity of 65%–70%, at 20 °C, the preparation decomposes, which has been clearly detected from the increase in the intensity of the absorption in the region of the stretching vibrations of the cellulose OH groups and the synchronous weakening of the spectral bands due to the nitrite ester. The weakening of the band at 1680 cm^{-1} is accompanied by its bathochromic shift. The spectrum recorded after brief treatment of the film with water or ethanol corresponds to chemically unaltered cellulose.

The results of the spectroscopic experiments have been confirmed by Grinshpan,¹⁵ who, whilst retaining Schweiger's method,¹⁶ precipitated cellulose nitrite from the N_2O_4 –acetonitrile system. According to these data, the 1660 and 1780 cm^{-1} bands were present in the IR spectrum of a film of the highly substituted product ($\text{DS} = 2.80$) and an appreciable absorption was noted in the range 3100–3500 cm^{-1} . The appearance of the latter as well as the displacement of the N=O bond stretching vibration band maximum from 1680 to 1660 cm^{-1} are most probably caused by the partial decomposition of the specimen during the experiments. Thus the presence of absorption bands at 1780 cm^{-1} and in the range 1650–1680 cm^{-1} must be regarded as specific characteristic of the IR spectrum of cellulose nitrite. This characteristic is common to all nitrite esters.^{57, 60}

The formation of cellulose nitrite in the above systems, and not of its complexes with nitrogen oxides,^{15, 27, 36, 61} has been confirmed also by the results of the analysis of the solutions for HNO_3 , the second product of the esterification reaction. The amount of HNO_3 was determined from the mass of the pyridinium nitrate precipitated when an excess of pyridine was added to a solution of cellulose in the N_2O_4 –ethyl acetate mixture. Absolute diethyl ether, which is incapable of precipitating the polymer, was used in addition to isolate pyridinium nitrate from the N_2O_4 –DMF system. According to the experimental data approximately 3 moles of HNO_3 per glucopyranose unit (GPU) of cellulose are present in the solutions, i.e. as much as should have been obtained on total esterification of cellulose.

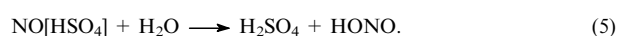
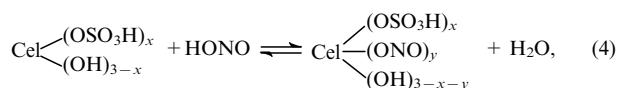
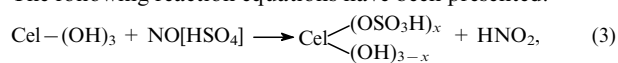
It has been suggested¹⁴ that the presence of a strong organic base is obligatory for the *O*-nitrosation of cellulose, because cellulose nitrite can be isolated from solution only with participation of amines.^{16, 44, 46, 48} Developing further this hypothesis,

Grinshpan¹⁵ attributes to amines the role of a catalyst in the esterification of cellulose by the nitrous acid formed when the nitrogen oxides of the solvent mixture interact with water in the precipitation baths. It has been suggested that, apart from the catalytic effect, the presence of amines prevents the decomposition of HNO_3 . The cause of the high content of nitrite ester groups ($\text{DS} = 2.50$ –2.95) in the deposits isolated without the use of water was not discussed in this connection.^{46, 48}

The catalytic function of amines is confirmed, according to Grinshpan's data,¹⁵ by the procedure described in a inventor's certificate.⁶² According to this procedure, cellulose nitrite can be precipitated from solutions at the instant of formation by employing a cooled water–pyridine mixture. It was noted that the cellulose nitrite isolated from solutions incorporating an organic component with a lower proton affinity (ethyl acetate or acrylonitrile and not DMF or DMSO) is the most stable. This factor is assessed as an argument in support of the dissolution of cellulose without esterification to the nitrite. It has been stated that if an esterification had occurred, the product isolated from solution in DMF or DMSO would be more stable. However, it is evident that in the presence of amines, the proton affinity towards the solvent loses its importance and an effect of 'protection' of cellulose nitrite against water should be manifested in more hydrophobic media (of the type of ethyl acetate).

The possibility of the *O*-nitrosation of cellulose, even in the absence of amines on its dissolution in nitrosyl-containing systems with a 'dual' esterifying ability: $\text{NO}[\text{HSO}_4]$ –DMF, $\text{NO}[\text{SbCl}_6]$ –DMSO, has been assumed.¹⁵ According to the author, the anionic components of the salt-like compounds in such systems perform simultaneously the functions of esterifying agents, *O*-nitrosation acid catalysts, and stabilisers of the HNO_2 and the cellulose nitrite formed.

The following reaction equations have been presented:



The nitrite ester groups in the mixed cellulose ester formed are fairly stable.^{45, 46, 48} A substantial part of them ($DS = 1.21$) can be detected together with sulfate groups ($DS = 1.19$) in the deposits isolated at 20 °C by means of acetone without using amines.⁴⁵ On the other hand, the content of nitrite groups in the deposits obtained by similar procedures from the N_2O_4 -DMF and $NOCl$ -DMF solvent systems is very small, which, according to Grinshpan,¹⁵ confirms the absence of reactions similar to reactions (3)–(5) and the constancy of the chemical composition of the cellulose dissolved in these media. However, even if the latter possess a nitrosating activity, one cannot expect a high concentration of nitrite ester groups in the products precipitated with acetone, in which the highly substituted cellulose nitrite is readily dissolved.^{15, 57} The ability of ketones to enolise in acid media induces denitrosation and hence the deposition of the polymer. When N_2O_4 is combined with acetone, a stable solution cannot be obtained because of enolisation.

The majority of investigators^{37, 40, 41, 44, 46, 51, 52, 63, 64} attribute the dissolution of cellulose to the esterifying ability of nitrosyl-containing compounds (in the first place N_2O_4) in the absence of amines. Other views on this process have been expressed in studies^{15, 27, 36, 61} in which the postulated compositions and structures of the molecular complexes, ensuring, according to the authors, the dissolution of cellulose, are discussed. The results of the analysis of the solutions by UV,^{15, 57, 59} IR,^{15, 24, 59, 65} ^1H NMR,^{15, 51} and ^{13}C NMR^{15, 49} spectroscopic methods as well as calorimetry^{15, 63} have been treated in a contradictory manner by the supporters and opponents of the nitrite mechanism of the dissolution of cellulose. The IR spectra of the Cel- N_2O_4 -DMSO system (Fig. 2) contain evident features of the esterification of cellulose, such as the decline of the intense absorption in the range 3100–3500 cm^{-1} and the appearance of bands characteristic of the nitrite ester substituents introduced into the chain (at 1650 and 730 cm^{-1}).^{24, 57, 65} The dissolution of the model cellulose nitrite in DMSO induces a shift of the $N=O$ bond stretching vibration band maximum from 1680 to 1660 cm^{-1} , while the position of the band at 780 cm^{-1} is retained. A similar phenomenon has been observed also for low-molecular-mass nitrites in polar solvents.⁶⁶ The position of the absorption band of pentyl nitrite at 1650 cm^{-1}

remained unchanged after dissolution in CCl_4 , but was displaced to 1630 cm^{-1} after dissolution in $CHCl_3$.

Analysis of the IR spectra obtained in a number of studies^{24, 57, 65} (Fig. 2) showed that the spectrum of the Cel- N_2O_4 -DMSO system can be regarded, with some approximation, as a superposition of the spectra of solutions of cellulose nitrite and HNO_3 in DMSO. The absorption maxima of the dissolved cellulose nitrite (1660 cm^{-1}) and HNO_3 (1640 cm^{-1}) are not then resolved. For the Cel- N_2O_4 -DMSO system, they are averaged out at about 1650 cm^{-1} .

The use instead of cellulose of its analogue soluble in DMSO, namely starch, makes it possible to trace the variation of the absorption under the influence of N_2O_4 in the region of the stretching vibrations of the OH groups of the polysaccharide (Fig. 3). The addition of N_2O_4 to a solution of starch (up to 3 moles per GPU) induces a pronounced weakening of the intensity of the absorption band due to the OH groups. The bathochromic shift of this band (from 3310 to 3240 cm^{-1}) taking place simultaneously with the changes in intensity can be logically explained by the different reactivity of the reaction of the OH groups, depending on the energy of the hydrogen bonds, similar to that in the synthesis of the nitrites of other polyols.⁵⁸ A number of the most strongly bound hydroxy-groups remain free. An increase in the N_2O_4 concentration in solution also leads to a steady intensification of the spectroscopic indications of the presence of starch nitrite (bands at 1650 and 780 cm^{-1} and HNO_3 , (2100–2600, 1340 820, and 620 cm^{-1}). In the measurement of the IR spectra of solutions, it is necessary to take into account the high sensitivity of the preparation in the form of a thin liquid layer to atmospheric moisture. The increase in the intensity of the absorption band of the cellulose OH group is the spectroscopic evidence of the rapid decomposition of cellulose nitrite.

According to Grinshpan,¹⁵ the IR spectra of the Cel- N_2O_4 -DMSO system do not conflict with the hypothesis that cellulose dissolves via the formation of a Cel-organic solvent- NO_2 ternary complex. The reasons for the marked weakening of the absorption intensity in the range 3100–3500 cm^{-1} are not discussed. It is postulated that the bands at 1650 cm^{-1} (at 1640 cm^{-1} according to Grinshpan¹⁵) and 1340 cm^{-1} (Fig. 2)

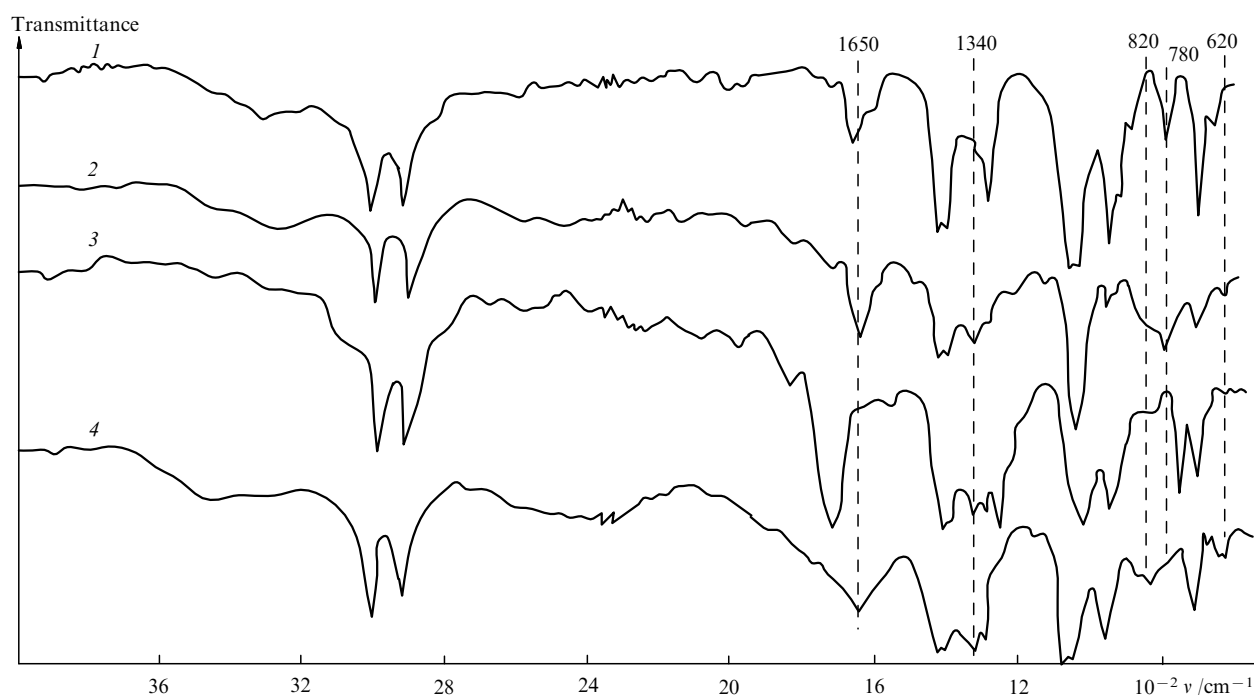


Figure 2. IR spectra of a 15% solution of cellulose nitrite ($DS = 2.85$) in DMSO (1) of the Cel- N_2O_3 -DMSO (10:17:73 mass %) homogeneous system (2), and of the N_2O_4 -DMSO dissolving mixture (3) and of 11.6 mass % HNO_3 solution in DMSO (4).

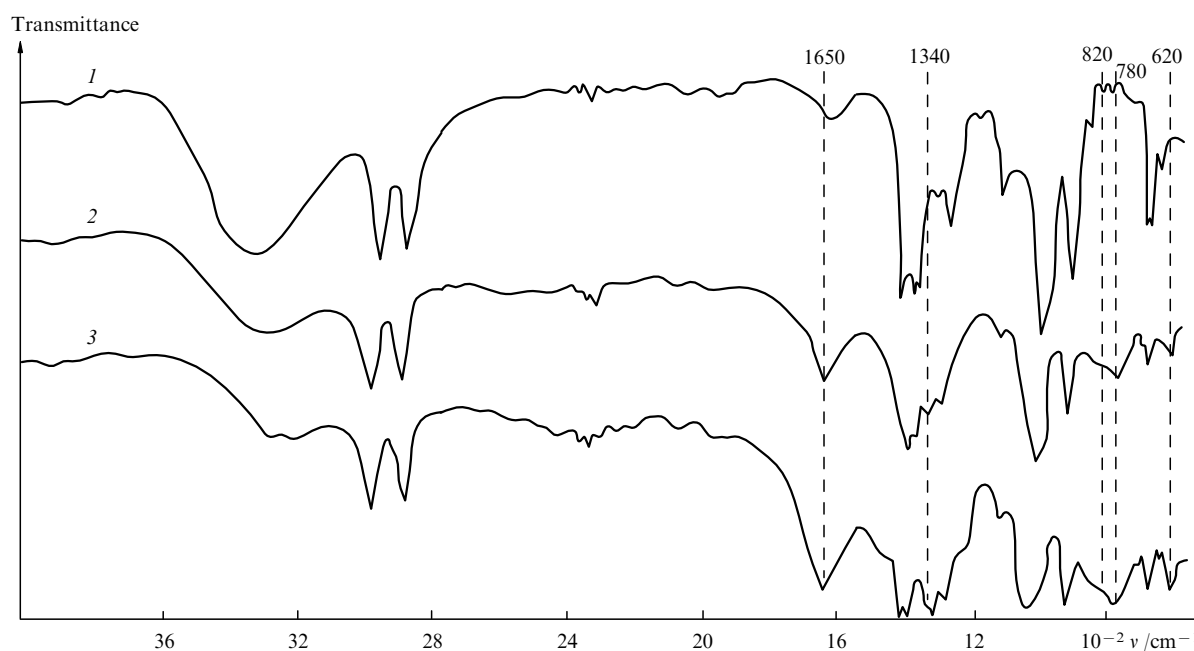


Figure 3. IR spectra of an 8% solution of starch in DMSO (1) and of the same solution to which two (2) and three (3) moles of N_2O_4 per GPU have been added.

are due to the NO_2 molecules bound in a complex with DMSO. This explanation is not based on any known reference guidelines similar to those in the spectra of low-molecular-mass nitrites. For systems incorporating nitrogen oxides with different degrees of oxidation and the products of their heterolytic dissociation (nitric and nitrous acids), the controversial character of such assignments of the spectral bands is evident. The explanation of the appearance of the 780 cm^{-1} band by the formation of a nonchemical sorption compound of cellulose and anhydrous HNO_2 is likewise controversial. The latter arises in the system ‘...on homogeneous dissociation of a C–H bond in the alcoholic groups of cellulose effected with the aid of the NO_2 radical molecules’.¹⁵ The origin of the bands at 1420 , 1300 , and 940 cm^{-1} is also attributed to the formation of a stable $\text{Cel}-\text{HNO}_2$ sorption complex. However, the intensity of precisely these bands in the spectrum of a solution of starch in DMSO is appreciably higher than in the spectrum of the same solution containing N_2O_4 (Fig. 3). The explanation of a series of observations in Grinshpan’s study,¹⁵ which follows from the known similarity of certain spectral features of HNO_2 and organic nitrites, repeats essentially the hypothesis previously tested by Ermolenko²⁸ and rejected.

Philipp and coworkers,^{17,45–50} who have investigated extensively the state of cellulose in nitrosyl-containing solvent systems, allow (in the papers by Nehls et al.⁴⁹ and Philipp et al.⁵⁰) the possibility of equilibrium between the cellulose nitrite ester and its adduct with N_2O_4 via a subsidiary valence. This conclusion was based on the analysis of ^{13}C NMR spectra of the $\text{Cel}-\text{N}_2\text{O}_4-\text{DMF}$ system,⁴⁹ indicating at least partial esterification. It has been noted^{49,50} that the introduction of amines promotes a shift of the equilibrium towards full esterification and the isolation of a product similar in composition to cellulose trinitrite.

III. Studies on the heterogeneous *O*-nitrosation of cellulose and its products

A comprehensive study of cellulose nitrite became possible after a way had been found of preparation it without impurities in a dry crystalline state. It has been suggested that mixtures of N_2O_4 with aprotic organic liquids, which do not dissolve cellulose nitrite, be used for the *O*-nitrosation of cellulose.^{57, 64, 67–71} As in the preparation of solutions, the ‘driving force’ of the process is the

increased affinity of the reaction medium for HNO_3 . The use of DMF, DMSO, DMA, and ethyl acetate is possible only in the presence of an excess of N_2O_4 ($> 30\text{ vol.}\%$), which rules out the dissolution of the reaction product. Absolute diethyl ether, which does not dissolve cellulose nitrite, proved to be the most suitable organic component. Diethyl ether has a fairly high affinity for HNO_3 ^{72,73} (Table 1) and N_2O_4 ;^{74,75} it is suitable not only as a reaction medium but also as a medium for the subsequent removal of the sorbed nitrogen-containing substances from the final product. The high vapour pressure of diethyl ether ensures the ease and completeness of the drying of cellulose nitrite washed with this solvent.

In the study of the nitrosating activity of the N_2O_4 diethyl ether system it was established^{68,70} that, with increase in the

Table 1. The donor numbers (DN) of the organic solvents employed and the enthalpies of their interaction with HNO_3 ($-\Delta H$).

Solvent	DN	$-\Delta H/\text{kJ mol}^{-1}$
Pyridine	33.1	99.2
DMSO	29.8	52.5
DMF	26.6	60.2
Diethyl ether	19.2	29.8
Ethyl acetate	17.1	19.7

concentration of N_2O_4 in the mixture to $\sim 23\text{ vol.}\%$, the increase in the rate of reaction is small. This is followed by acceleration, which becomes very rapid starting from N_2O_4 concentration of $\sim 37\text{ vol.}\%$ (Fig 4). These N_2O_4 concentrations actually correspond to the stoichiometric molar compositions (1 : 2 and 1 : 1) of its complexes with diethyl ether.⁷⁵ As a consequence of the decomposition of the complexes, the system contains a certain amount of free N_2O_4 , which permeates into the bulk of the fibre much more readily than the complexes. The 1 : 1 complex is less stable⁷⁵ and more dissociated. With increase in the N_2O_4 concentration above the stoichiometric value, the nitrosation process accelerates sharply. An increase in temperature tends to decrease the stability of the complexes with ‘liberation’ of N_2O_4 and its dissociation.⁷⁵ The reaction rate increases more than might have

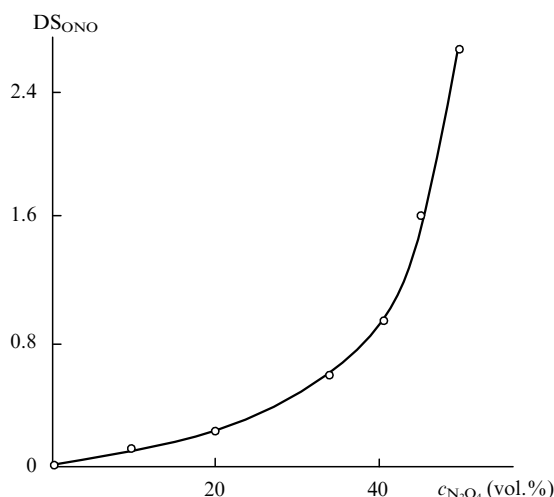


Figure 4. Dependence of the degree of nitrosation of cellulose on the N_2O_4 concentration in diethyl ether (reaction time 18 min, liquid modulus 50 ml g^{-1} , 0°C).

been expected solely on the basis of the temperature coefficient of diffusion.^{68,70} Taking into account the high volatility of the components of the nitrosating mixture, it was recommended^{67,68,70} that cellulose trinitrite be obtained in the presence of a higher N_2O_4 content ($\sim 50 \text{ vol. \%}$) in diethyl ether but at reduced temperatures ($\sim 0^\circ\text{C}$). The final product should be washed free of the sorbed components of the reaction medium with cooled absolute diethyl ether, the completion of the washing process being checked by means of the starch-iodine indicator. It is desirable that the preparation be dried by evacuation in the cold.

The nitrosation of cellulose takes place also in the absence of an electron-donating organic component.^{68,69} The excess N_2O_4 is capable of binding and removing from the reaction zone the HNO_3 produced, since it dissolves it with formation of fairly stable compounds.⁷⁶ The rapid intracrystallite permeation of the free N_2O_4 into the cellulose phase gives rise to a very high rate of reaction.⁶⁹ However, serious methodological, complications, associated with the occurrence of competing processes, arise in this case.⁶⁹

The combination of diethyl ether with NOCl does not allow the preparation of a highly substituted cellulose nitrite.^{57,68} The electron-donating ability of diethyl ether is insufficient to bind the hydrogen chloride formed as a side product, which is a stronger acid than HNO_3 . A mixture of chloroform with pyridine is suitable in this instance as the reaction medium. In contrast to diethyl ether, chloroform can dissolve and remove from the reaction zone the second reaction product, pyridine hydrochloride.

The sorbed components of the reaction medium can be removed from the reacted material also with water at $0-5^\circ\text{C}$ in the presence of bases such as, for example, pyridine or NaHCO_3 ($\text{pH} \sim 8.5$).^{57,69} A moist fibrous cellulose nitrite, stable in the cold and similar to the preparations isolated from solutions, is obtained.^{44,59}

Analysis of the products of the heterogeneous reaction for the nitrite and nitrate forms of nitrogen by the familiar chemical methods and also those proposed by Torgashov and co-workers,^{57,59,68} demonstrated a satisfactory agreement among the results, indicating the vast predominance of the nitrite ester groups and the possibility of the attainment of a high degree of substitution up to complete substitution. Using the gravimetric analysis of a dry preparation ($\text{DS} = 2.97$) obtained with the aid of diethyl ether from chromatographic paper (97% α -cellulose), Torgashov et al.⁵⁷ tested, apart from the conclusion about the purity of the product, the hypothesis^{15,36,61} that molecular complexes between cellulose and HNO_2 or nitrogen oxides with

different degrees of oxidation are formed in the given systems. After nitrosation, washing, drying and regeneration, the specimen retained the form of a sheet, which is most convenient for studies. The molecular mass (M) of the elementary unit of the nitrogen-containing compound obtained was found from the gravimetric results:

$$M = 162 \frac{m_1}{m_2},$$

where m_1 and m_2 are the masses of the reaction product and of the cellulose regenerated from it with water. The value $M = 249.48$ found was compared with the molecular masses of the postulated compounds (Table 2). The latter were calculated from the degree of substitution in terms of HNO_2 . The minimum discrepancy between the experimental and calculated values corresponds to cellulose nitrite ($\text{DS} = 2.97$). For the remaining variants, the discrepancy greatly exceeds the possible errors of the gravimetric method. The formation of cellulose nitrite in the given systems and not of its isomeric *C*-nitroso-compound is demonstrated by the decomposition of the preparations obtained by LiAlH_4 or CaH_2 in anhydrous diethyl ether into ammonia and chemically unchanged cellulose.⁵⁷ *C*-Nitroso-compounds are known to be readily reduced to amino-derivatives.

The visible and UV spectra of the preparations obtained are identical with the spectra of the cellulose nitrite isolated from

Table 2. The calculated molecular masses of postulated compounds of different composition.

Compound	M	Absolute deviation	Relative deviation (%)
$\text{C}_6\text{H}_7\text{O}_2(\text{OH})_{0.03}(\text{ONO})_{2.97}$	248.13	+1.35	0.5
$\text{C}_6\text{H}_7\text{O}_2(\text{OH})_3 \cdot 2.97\text{HNO}_2$	301.59	−52.11	20.9
$\text{C}_6\text{H}_7\text{O}_2(\text{OH})_3 \cdot 2.97\text{N}_2\text{O}_4$	435.24	−185.76	74.5
$\text{C}_6\text{H}_7\text{O}_2(\text{OH})_3 \cdot 2.97[\text{N}_2\text{O}_4 \cdot (\text{C}_2\text{H}_5)_2\text{O}]$	655.02	−405.54	162.5
$\text{C}_6\text{H}_7\text{O}_2(\text{OH})_3 \cdot 1.485\text{N}_2\text{O}_3$	274.86	−25.38	10.2

Note. The absolute and relative deviations are quoted relative to the experimental molecular mass M of 249.48.

solution⁵⁹ and with the spectra of other organic nitrites (Fig. 5). The 4–5 band absorption in the range 330–380 nm characteristic of these compounds⁶⁶ vanishes when the preparation is treated with water or alcohol. A similar correspondence has been observed between the IR spectra of the heterogeneous interaction products and the highly substituted cellulose nitrite precipitated from solution.^{15,59} The spectrum of a solution of cellulose in DMSO presented in Fig. 2 corresponds to the preparation obtained with the aid of diethyl ether.

In a study of the crystal structure of cellulose trinitrite,^{68–70,77–80} special procedures,^{68,69,79} ensuring the protection of the specimen against decomposition throughout the X-ray diffraction measurement, were used. Oriented preparations ($\text{DS} = 2.93-2.97$) were obtained from purified and bleached flax fibres (97% α -cellulose), which had been used successfully in previous^{81,82} X-ray diffraction analyses of cellulose nitrates.

The texture X-ray diffraction pattern of cellulose trinitrite (Fig. 6), (Table 3) contains 19 independent reflections, which have been satisfactorily indexed in terms of a monoclinic unit cell with the parameters $a = 25.3 \text{ \AA}$, $b = 18.9 \text{ \AA}$, $c = 25.5 \text{ \AA}$ (fibre axis), and $\gamma = 95.8^\circ$.^{70,79} Eight chain molecules pass through the unit cell. The theoretical density of the crystallites, calculated from these unit cell parameters, is 1.36 g cm^{-3} . The experimental density (1.39 g cm^{-3}), determined pycnometrically using absolute diethyl ether, agrees satisfactorily with the calculated value. In the determination of the density, the operations involving the nitrosation of cellulose with a N_2O_4 –diethyl ether mixture and

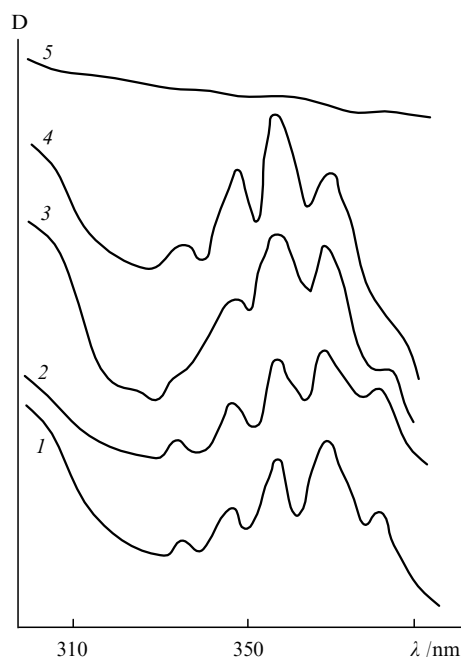


Figure 5. UV and visible spectra of *tert*-butyl nitrite (1), glycerol trinitrite (2), poly(vinyl alcohol) nitrite (3), cellulose nitrite (DS = 2.85) (4), and cellulose nitrite (DS = 2.85) after its interaction with alcohol (5).

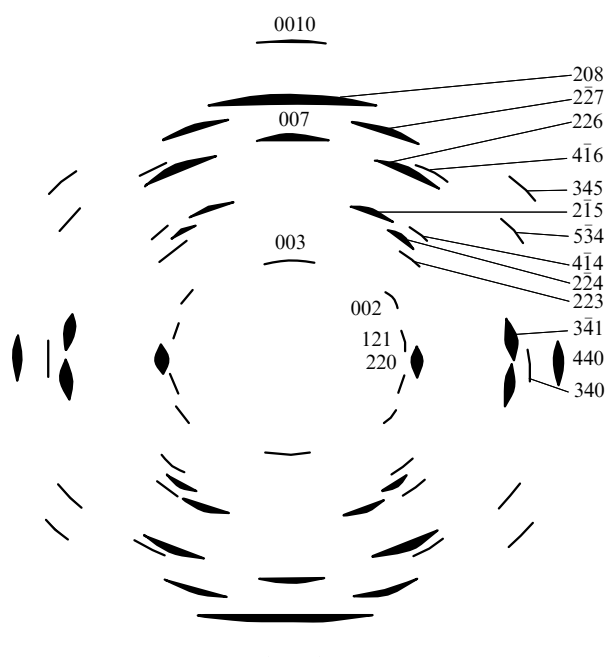


Figure 6. The indexing of the reflections on the texture X-ray diffraction pattern for cellulose trinitrite (DS = 2.97).

the washing of the final product with diethyl ether were performed directly in the pyknometer.^{70, 79}

There is an evident analogy between the structures of the cellulose trinitrite crystallites and those of the 'related' cellulose trinitrate.^{81–83} Both compounds are outstanding among the crystallographically investigated cellulose derivatives having a helical chain conformation with a five-unit pitch and hence with an 'anomalous' identity period of ~ 25.5 Å. In the crystallites of other cellulose triesters as well as cellulose itself, this parameter is

Table 3. The observed reflections and interplanar spacings (d) of cellulose trinitrite crystallites (Cu $K\alpha$ radiation, Ni filter).

hkl	$d/\text{Å}$		I^a
	experiment	calculation	
220	7.10	7.19	v.s.
340	3.90	3.93	v.w.
440	3.55	3.59	s.
121	8.03	8.07	w.
$3\bar{4}1$	4.28	4.23	v.s.
022	7.55	7.57	v.w.
003	8.51	8.48	w.
223	5.40	5.49	w.
224	4.93	4.97	m.
$4\bar{1}4$	4.43	4.43	w.
$5\bar{3}4$	3.49	3.47	v.w.
$2\bar{1}5$	4.66	4.63	m.
345	3.13	3.11	v.w.
$2\bar{2}6$	3.74	3.75	s.
$4\bar{1}6$	3.50	3.50	w.
007	3.65	3.60	m.
$2\bar{2}7$	3.31	3.33	m.
208	3.09	3.09	m.
010	2.55	2.55	v.w.

^a The following designations for the intensities of the reflections have been adopted: v.s. — very strong; s. — strong; m. — medium; w. — weak; v.w. — very weak.

determined by the length of the cellulose fragment (~ 10.3 Å) regardless of the polymorphic modification.

Distinctive features have also been noted in the formation of the crystalline phases of the incompletely substituted nitrated and nitrosated cellulose.⁶⁹ The different contents of nitrogen in specimens of highly substituted cellulose nitrate causes certain differences in the unit cell parameters.^{4, 82} Accordingly, the angular distribution of the reflections on the X-ray diffraction patterns of preparations with high but somewhat different degrees of substitution may not agree. In the case of cellulose nitrite, the dependence of the diffraction angles on the degree of substitution, the nature of the nitrosating agent (N_2O_4 or NOCl), and other factors is almost imperceptible.⁶⁹ On the diffractograms of preparations differing, apart from the degree of substitution (2.52–2.85), in the form of the initial native cellulose, the nitrosation conditions, and the conditions in the isolation of the product from the reaction mixture, the angular positions of the reflections are identical and the same as for cellulose trinitrite (Fig. 7). The above factors influence mainly the intensity and sharpness of the reflections.

For the same degree of substitution and preparation conditions, the nitrite of wood cellulose is consistently less crystalline than the nitrite of cotton or flax cellulose, since the crystal structure of its cellulose precursor is less ideal. The crystallinity of the cellulose nitrite obtained in diethyl ether, which is inert to it, is always higher than that of the preparation obtained in DMF or ethyl acetate, which do not dissolve this product solely by virtue of the excess of N_2O_4 in the system. The crystallinity of equally substituted cellulose nitrosation products increases in aliphatic carboxylic acids with increase in the length of the hydrocarbon group of the acid. The isolation of cellulose nitrite from the reaction medium with the aid of anhydrous CCl_4 or CH_2Cl_2 , which are indifferent to N_2O_4 and HNO_3 , is accompanied by a decrease in the degree of substitution and crystallinity. In contrast to diethyl ether, these liquids do not have a stabilising effect and serve merely as a 'transporting agent' in the removal of excess reactants from the polymer phase. The quite distinct individuality of the diffractogram of cellulose nitrite makes it possible to employ the X-ray diffraction method for the detection of the

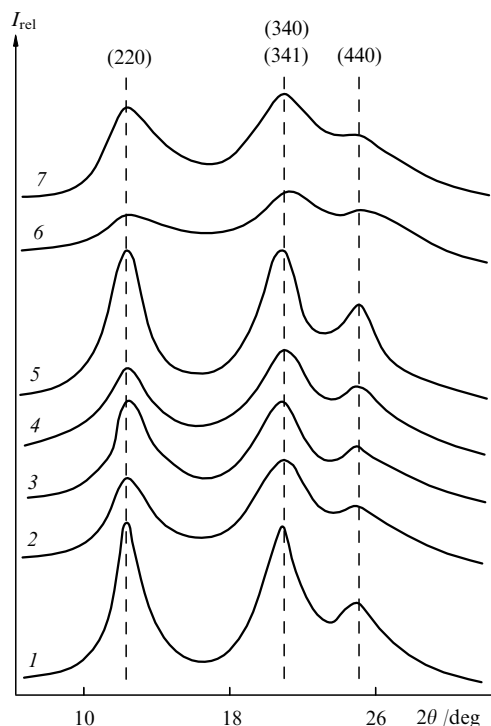


Figure 7. Diffractograms for isotropic cellulose nitrite specimens. Specimen: (1) DS = 2.85, obtained from cotton cellulose in N_2O_4 –diethyl ether, isolated with diethyl ether, and dried *in vacuo*; (2) DS = 2.78, obtained from wood cellulose in N_2O_4 –ethyl acetate, isolated with diethyl ether, and not dried; (3) DS = 2.81 obtained from cotton cellulose in N_2O_4 –DMF, isolated with a water–pyridine mixture, and not dried; (4) as (3), but isolated with NaHCO_3 solution; (5) DS = 2.80, obtained from flax cellulose in N_2O_4 –caprylic acid, and not dried; (6) DS = 2.52, obtained from cotton cellulose in N_2O_4 –DMF, isolated with CCl_4 and CH_2Cl_2 in succession, and dried *in vacuo*; (7) DS = 2.75, obtained from cotton cellulose in NOCl – CHCl_3 –pyridine, isolated with a solution of pyridine in CHCl_3 , and not dried.

crystalline phase of this compound in a complex reaction mixture, where other methods are inapplicable.^{77,78}

The kinetics of the heterophase *O*-nitrosation of cellulose in organic media have been investigated taking into account the influence on the process exerted by the factors specific to the given systems.^{68,70,84,85} Together with highly crystalline cellulose, a specimen with a more accessible structure, prepared by the decrystallisation of cellulose, was employed. It was obtained by heterogeneous regeneration from cellulose nitrite under anhydrous conditions.⁸⁴ The reaction in DMF, ethyl acetate, diethyl ether, and acetic and oenanthic acids (AA and OA respectively) was investigated. The kinetic curves (Fig. 8) were obtained for the minimal value of the liquid modulus established (50 ml g^{-1}), an increase in which hardly affects the degree of esterification.

The long linear section of the curves, reflecting the constancy of the rate at which an appreciable mass of cellulose (from 40% to 90%) is converted into the nitrite, is described by the zero-order equation

$$\alpha = k_0 t,$$

where α is the degree of conversion at time t and k_0 is the rate constant.

In heterogeneous reactions, this type of relation is attributed to the constancy of the reaction surface in the conversion of a large proportion of the initial substance.⁸⁶ Bearing in mind that the capillary mechanism of the transport of the reactant predominates in cellulose fibres over the diffusional mechanism,⁸⁷ the constancy of the cross-section of the reactant flux may be represented as the migration of the reaction zone at a constant rate via a network of

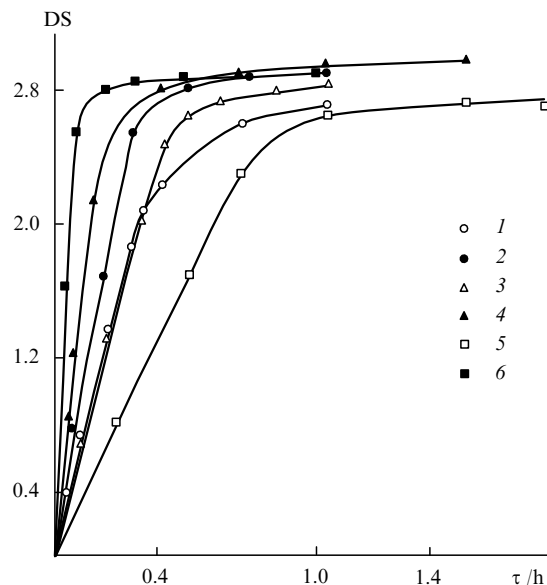


Figure 8. Kinetics of the heterophase nitrosation of cellulose under various conditions.

(1) N_2O_4 –oenanthic acid (20 : 80), 26.5 °C; (2) N_2O_4 –acetic acid (20 : 80), 26.5 °C; (3) N_2O_4 –DMF (50 : 50), 0 °C; (4) N_2O_4 –diethyl ether (50 : 50), 0 °C; (5) and (6) amorphised cellulose, N_2O_4 –diethyl ether (10 : 90), 0 and 26.5 °C respectively.

capillaries. In this case, one has to assume that the reaction proceeds layer-by-layer with conversion of the main bulk of cellulose on the outer surface. The decrease in the area of the latter is responsible for the bending of the kinetic curve on passing to inner regions, accessible with difficulty, where truly diffusional transport plays the main role.

Taking into account the methodology of the familiar studies^{88,89} on the topochemical reactions of cellulose, the experimental data (Table 4) were expressed quantitatively with the aid of the Erofeev–Kolmogorov equation

$$\alpha = 1 - \exp(-Kt^n),$$

where K and n are constants. The reaction orders n , determined from the slopes of the modified curves, indicate that the order is in all cases limited by chemical factors. The activation energies E are also too high for diffusional kinetics.⁹⁰ However, the inconstancy of the composition of the reaction mixture and of the state of the reacting surface, characteristic of the given systems, throw doubt on the conclusion concerning the rate-limiting stage reached from the analysis of topokinetic equations. The influence of the nature of the solvent and temperature on the rate of the complex formation reaction between the liquid components^{74,75} was discussed above. The rate of the reaction depends on the nature of the organic medium even in mixtures rich in N_2O_4 (Table 4). The smallest change in the reaction surface as a result of swelling should occur during nitrosation in diethyl ether and acetic and oenanthic acids, which do not dissolve cellulose nitrite. The rate of reaction in diethyl ether, the basicity of which is higher than that of carboxylic acids, is higher than in acetic acid but lower than in oenanthic acid, although the basicities of both acids are virtually identical. This difference can be accounted for by taking into account the functional density of the medium (FDM), equal to the number of electron donors per unit volume.⁸⁴ The expression for this parameter includes the density (d , at 20 °C) and the molecular mass of the organic liquid:

$$\text{FDM} = \frac{1000d}{M}.$$

Table 4. The conditions and kinetic parameters of the cellulose *O*-nitrosation reaction.

$c_{N_2O_4}$ (vol. %)	$T/^{\circ}C$	$A(\%)^a$	k_0/h^{-1}	k/h^{-1}^b	n	E / kJ mol ⁻¹ c
Organic medium — diethyl ether						
50	0	80	3.70	7.50	1.21	
40	0	75	1.07	2.26	1.36	
33	0	70	0.67	1.05	1.00	
20	0	70	0.26	0.41	1.25	64; 69
20	11.5	76	0.71	1.34	1.17	
20	15.0	75	1.10	2.21	1.30	
20	25.5	77	3.00	5.54	1.21	
10	0	40	0.05	0.07	1.02	79; 77
10	11.0	59	0.20	0.26	1.03	
10	25.5	67	0.88	1.34	1.14	
10	0 ^d	82 ^d	1.15 ^d	2.17 ^d	1.25 ^d	54 ^d ; 58 ^d
10	25 ^d	90 ^d	8.50 ^d	19.70 ^d	1.21 ^d	
Organic medium — ethyl acetate						
50	0	70	1.43	2.22	1.06	
Organic medium — acetic acid						
50	0	60	1.58	2.70	1.20	
68	0	73	7.73	11.83	1.27	
62	0	70	4.00	7.32	1.23	
20	0	67	0.13	0.19	1.10	80; 81
20	26.5	83	3.13	6.18	1.38	
Organic medium — oenanthic acid						
20	0	73	0.17	0.27	1.16	70; 68
20	26.5	70	2.33	3.30	1.08	
40	0	74	3.77	7.90	0.94	
30	0	67	1.83	4.52	1.53	
Organic medium — DMF						
20	0	—	~4	—		60
20	0	—	~24	—		
50	0	77	2.18	3.75	1.15	

^a The fraction of cellulose reacting in accordance with the equation $\alpha = k_0 t$. ^b Determined from K/h^{-n} with the aid of the Sakovich equation: $k = nK^{1/n}$. ^c Calculation by the Arrhenius equation; the first value corresponds to the values of k_0 . ^d Values for specimens of amorphised cellulose.

The smallest number of moles per unit volume is actually a characteristic of oenanthic acid (Table 5), so that a greater fraction of N_2O_4 remains unbound in the latter compared with other media. The activation energy is higher in mixtures of N_2O_4 with acetic acid than in its mixtures with oenanthic acid (Table 4), since the dissociation of the complex is an endothermic process⁷⁴ and the FDM is higher for acetic acid. Accordingly, with increase in temperature the reaction in acetic acid is accelerated to a greater extent than in oenanthic acid. The viscosity of the medium also plays an important role; the viscosity of oenanthic acid is highest (Table 5). In mixtures of diethyl ether, acetic acid and oenanthic acid with a reduced N_2O_4 content, where the influence of the FDM is abolished by the excess of the solvent, the importance of

transport factors increases. In the least viscous, diethyl ether, the rate of reaction at a relatively low N_2O_4 concentration (20 vol. %) is higher than in oenanthic acid medium of similar composition.

The influence of the structural characteristics of cellulose on the process kinetics is manifested clearly in experiments with a decrystallised specimen.⁸⁴ As a consequence of the facilitation of mass transport, there is a significant increase in the rate constant and in the fraction of cellulose reacting at a constant rate, as the activation energy diminishes (Table 4). In DMF and ethyl acetate, which dissolve cellulose nitrite, a heterogeneous course and completion of the reaction are possible only in the presence of an excess of N_2O_4 (40 vol. % – 50 vol. %). The decrease in its concentration as a result of its consumption on nitrosation alters the nature of the interface, since the polymer swells. The reason for the hindrance of mass transport may be the formation of a gel-like layer, the viscosity of which is highest when ethyl acetate is employed.¹⁵ A distinctive feature of these systems is the acceleration of the reaction following a decrease in the N_2O_4 concentration to ~20 vol. % and its completion by the complete dissolution of the material. The baring of the reaction surface as a result of the dissolution of the reacted layer facilitates mass transport and accelerates the reaction (k_0 was estimated approximately in this case from the time for the total dissolution of the specimen).

The sensitivity of the reaction to factors which determine the transport of the reactant, the change in the properties of the reaction surface, and also the appreciably lower rate of interaction with N_2O_4 than for low-molecular-mass analogues⁹¹ conflict with the conclusion that chemical inhibition, which follows from the value $n \geq 1$, takes place. A precondition of an adequate description of the process is, in particular, that the composition and homogeneity of the polymer phase be determined at different stages of the reaction. Analysis of the corresponding diffractograms (Fig. 9) indicates convincingly the layer-by-layer course of the process, throughout which the material remains crystalline. The intensification of the reflections due to cellulose trinitrite with increase in the degree of substitution is accompanied by the

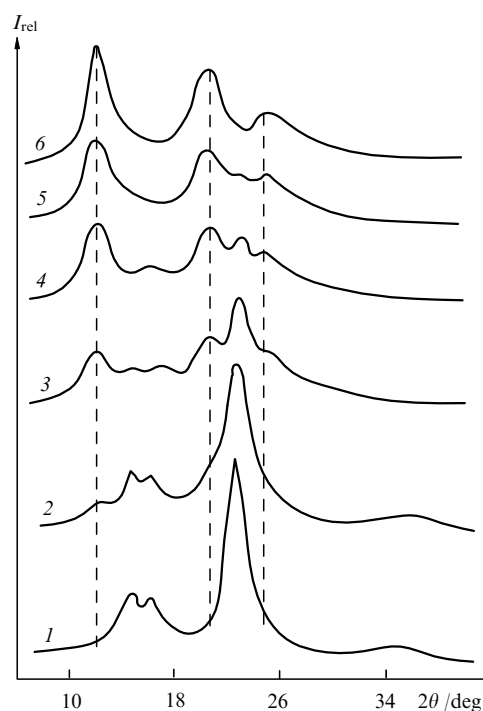


Figure 9. Dynamics of the structural rearrangement at different stages of the nitrosation of cellulose with a N_2O_4 – diethyl ether (50 : 50) mixture at 0 °C. DS: (1) 0.33; (2) 0.91; (3) 1.98; (4) 2.30; (5) 2.60; (6) 2.93.

Table 5. The functional densities of the medium (FDM) and the viscosities of the organic media employed.

Solvent	FDM/mol litre ⁻¹	η /cP
Diethyl ether	9.70	0.23
Acetic acid	17.50	1.21
Oenanthic acid	7.07	4.34
DMF	13.00	1.10
Ethyl acetate	10.21	0.46

synchronous weakening of the Cel-I reflections as far as their complete degeneration. The diffractograms of the products of the intermediate reaction stages resemble those of a mechanical mixture of the crystallites of Cel-I and its trinitrite. With the aid of ethyl acetate, which is indifferent to cellulose, it is possible to separate quantitatively a weakly substituted preparation ($DS = 1.53$) into a solution of highly substituted cellulose nitrite, and a virtually unaltered Cel-I.⁸⁴

These data, together with those examined above (Fig. 7) clearly indicate the direct formation of the triester from cellulose, i.e. a high rate of the chemical reaction proper. In the kinetic reaction regime, a nearly statistical substitution of the OH groups, inducing the diffuseness of the X-ray diffraction patterns of the partly substituted preparations, would be most probable. By definition,⁹⁰ the set of the above features makes it possible to identify the *O*-nitrosation of cellulose in electron-donating organic media as a process occurring under the conditions of strong internal-diffusion inhibition in the 'external kinetic region'. The reaction is 'displaced' on to the outer surface and proceeds in a regime simulating the kinetic regime.

The highly substituted cellulose nitrite obtained as a result of heterogeneous processes with the aid of diethyl ether is a white substance with a yellowish tint. Its form corresponds to that of the initial cellulose (fibre, sheet, powder). In a moist atmosphere, it decomposes, readily with evolution of nitrogen oxides. Its resistance to the action of moisture increases appreciably in the pressed state.⁶⁸ The decomposition process is retarded in alkaline media.⁷⁰ On ignition, cellulose nitrite burns vigorously. The enthalpies of combustion and formation of cellulose nitrite, determined calorimetrically in the absence of contact with atmospheric moisture, are respectively -2970 ± 12.5 and -391 ± 12.5 kJ mol⁻¹.⁹² The high heat of explosive decomposition (-3660 kJ kg⁻¹) and the large volume of the gases evolved on explosion (870 litre kg⁻¹) make it possible to classify cellulose nitrite as a fairly powerful explosive.

The N₂O₄- and HNO₃-free bright transparent solutions of cellulose nitrite in organic solvents are distinguished by a series of properties from the familiar solutions in nitrosating compositions.^{93–96} Their lower viscosity makes it possible to attain a high polymer concentration (up to 15%). For example, the viscosity of a 6% solution of the nitrite of sulfate cellulose (DP = 1200) in ethyl acetate corresponds to the viscosity of a 2% solution in the N₂O₄-ethyl acetate mixture.⁹⁴ A similar rule is characteristic also of solutions of cellulose nitrate incorporated in graft copolymers of cellulose. The stability of joint solutions of cellulose nitrite and synthetic and artificial polymers is higher than that of analogous systems incorporating N₂O₄ and HNO₃. The absence of N₂O₄ and HNO₃ makes it possible to employ polymeric additives sensitive to them (polyamides and rubbers), expanding the possibilities for the moulding of the composite materials.⁹⁵

Torgashov et al.⁹⁷ investigated the oxidation of cellulose nitrite ($DS = 2.80$) by N₂O₄ in carbon tetrachloride in order to test the hypothesis^{2,28} that the nitrite ester participates as an intermediate in the reaction of preparation of monocarboxycellulose. The model cellulose nitrite was oxidised much more slowly than cellulose itself. The onset of the oxidation process was preceded by an induction period of ~ 6 h, during which neither denitrosation nor oxidation took place (Fig. 10). The reaction of cellulose under the same conditions began with the accumulation of nitrite ester groups in the first ~ 10 min, after which the oxidation process developed and the content of the nitrite groups diminished.

The behaviour of the model cellulose nitrite and the nitrite formed in the Cel–N₂O₄–CCl₄ system is not equivalent owing to the formation in the latter case of HNO₃, which, together with the destabilisation of the nitrite ester, increases the electrophilicity of N₂O₄⁹⁸ and hence its oxidising capacity. If 100% HNO₃ (3 moles per GPU) is added to the reaction mixture during the oxidation of cellulose nitrite, modelling the Cel–N₂O₄ system thereby, the rate of accumulation of carboxy-groups is found to be even higher

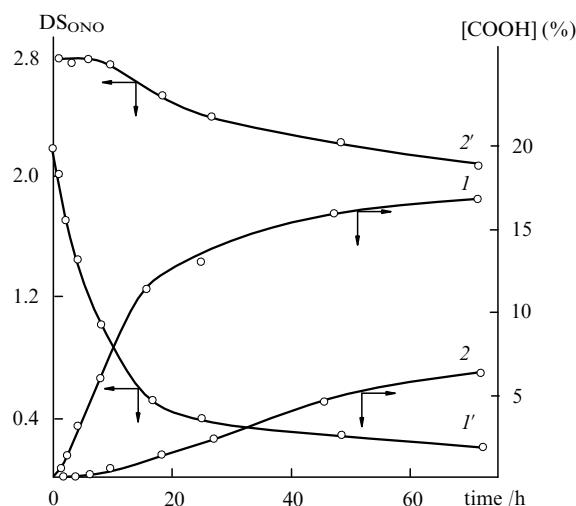


Figure 10. Variation of the contents of carboxy-groups (*I*, *2*) and nitrite ester groups (*I'*, *2'*) in the oxidation of cellulose (*I*, *I'*) and of its model nitrite ester (*2*, *2'*) with N₂O₄ in CCl₄.

than in the oxidation of cellulose. The formation of the labile cellulose nitrite at an intermediate stage of the oxidation process exerts a strong influence on the reaction, although, according to Sykes's data,⁹⁹ cellulose nitrite does not correspond to the intermediate in the cellulose oxidation reaction in terms of kinetic parameters.

IV. Heterophase structural transformations of cellulose with participation of labile nitrogen-containing derivatives

In the structural transformations taking place in the Cel–N₂O₄ system, the attention of investigators has been drawn to the effect of decrystallisation of native cellulose as a result of treatment with N₂O₄ and subsequent washing with water or an organic liquid.^{100–106} The use of both liquid^{101–105} and gaseous^{100–106} N₂O₄ for this purpose has been discussed. The chemical composition of the decrystallised cellulose is unaltered, but the DP diminishes significantly (as far as ~ 300).^{100,101,103} The degree of decrystallisation and the accompanying degree of transformation of the native structural form into the Cel-II form were found to be extremely sensitive to the moisture content of the initial fibre and the conditions employed to perform the both stages of the process.^{100,101,105,106} Such features of the process as the brief contact (~ 15 s) between cellulose and N₂O₄, which is sufficient for attainment of decrystallisation effect, or the suitability of water for washing of the treatment products, did not fit into the framework of the established ideas^{107–109} about the mechanisms of the heterophase amorphisation of cellulose by reagents capable of inducing its intracrystallite swelling.

The interaction of cellulose with a N₂O₄ solution (18 vol. %–20 vol. %) in glacial acetic acid and subsequent washing of the fibre with the same acid ensure the formation of an amorphous structure with a capillary-porous system developed to the maximum extent and accompanied by a much smaller decrease in DP.^{12,17,110,111} The cotton cellulose amorphised in this way is superior to the initial cellulose in terms of the water-retaining capacity (WRC) almost by a factor of 7 (250% against 37%).^{12,111} Under identical conditions in hydrolysis in dilute HCl, the amorphised cellulose loses 84% of its mass, while the initial cellulose loses only 35%.^{110,111} Complete acetylation of cotton cellulose after this treatment is 25 times faster than after standard activation with acetic acid alone.^{112,113} For cellulose decrystallised directly by N₂O₄, the superiority of these and some other

parameters over the initial ones is manifested to a much smaller extent.^{112, 114–117}

X-Ray-amorphous material with a high WRC ($\sim 250\%$) and a high hydrolysability has also been obtained by treating cellulose with more dilute (6 vol. %–10 vol. %) N_2O_4 solutions in acetic anhydride or mixtures of the latter with acetic acid.^{77, 118, 119} In contrast to the conditions indicated above, these reaction conditions induced the formation of a weakly substituted cellulose nitroacetate.

Kaputskii et al.¹²⁰ explained the amorphisation of cellulose by the irreversible destruction of the crystallites as a result of the intense swelling in the $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ dynamic mixture. A decisive role was attributed to physical factors — sorption, condensation, dimerisation of NO_2 molecules, disjoining effect. However, it was found from the results of X-ray diffraction phase analysis that the competitive formation of two new crystalline phases takes place in the swelling stage.^{121, 122} The X-ray diffraction expression for one of them corresponds to cellulose nitrite.⁶⁹ The second, more stable phase, is characterised by a diffraction pattern typical for Knecht's compound, the familiar adduct of cellulose with HNO_3 .³⁰ The ratio of these phases in the swollen fibre depends on the moisture content in the initial cellulose, on the treatment conditions, and in particular on the access of atmospheric moisture to the reaction zone.^{69, 121} The transformation of the structure of cellulose nitrite into that of KC under the influence of atmospheric moisture can be traced from the variation of the intensities of the corresponding reflections on the diffractograms of the fibre swollen in N_2O_4 .^{121–123}

The formation of cellulose nitrite in the reaction mixture was observed by X-ray diffraction^{10, 121, 122, 124–126} before the X-ray pattern of individual cellulose nitrite became known.⁷⁸ The cellulose nitrite phase has been erroneously classified^{10, 121, 122, 124–126} as a sorption compound on the basis of generally known principles^{108, 127} of the structural reorganisation of cellulose under the action of other active nitrogen-containing reagents (ammonia, amines, HNO_3), which induce its intracrystallite swelling. These studies initiated a detailed investigation of the structural transformations possible in the given system.

Each of the above phases can be formed separately (cellulose nitrite or KC) by establishing an appropriate regime in the interaction of cellulose with liquid N_2O_4 .^{69, 128, 129} If the reaction conditions promote the removal from the fibre of HNO_3 formed and prevent the access of moisture from the surrounding medium to the reaction zone, cellulose nitrite is formed preferentially. A preparation having a typical cellulose nitrite diffractogram (Fig. 11) has been obtained by the successive treatment of air-dry cellulose (moisture content 5%–7%) for ~ 2 min with three fresh portions of N_2O_4 whilst stirring and at a high value of the liquid modulus.^{69, 129} The rapid protection of the preparation from atmospheric moisture immediately on completion of the treatment is obligatory, since otherwise the reflections of the second phase (KC) appear on the diffractogram. The crystallinity of the cellulose nitrite thus obtained is always significantly lower than that of the substance obtained in the presence of an electron-donating liquid.

The combination of N_2O_4 with an electron-donating component (diethyl ether or acetic acid) pre-determines the nitrite pathway of the reaction and a higher stability of the cellulose nitrite swollen in the reaction medium.⁶⁹ On treatment with water, the crystalline phase of the nitrite of the native cellulose is readily reconverted into the crystalline Cel-I phase (Fig. 11).^{68–70, 129} A direct relation has been traced between the degrees of crystallinity of the regenerated Cel-I and the precursor (the nitrite ester). The use of hot water or steam for the hydrolysis of cellulose nitrite tends to increase the crystallinity of the regenerated Cel-I.^{68–70} The interconversion of the crystalline phases of Cel-I and its nitrite is characterised by more clear X-ray diffraction patterns than these obtained during the familiar heterogeneous cellulose esterification processes (acetylation, nitration) and in the hydrolysis of its triesters.¹³⁰ The conclusion¹³⁰ that the lattices of the initial

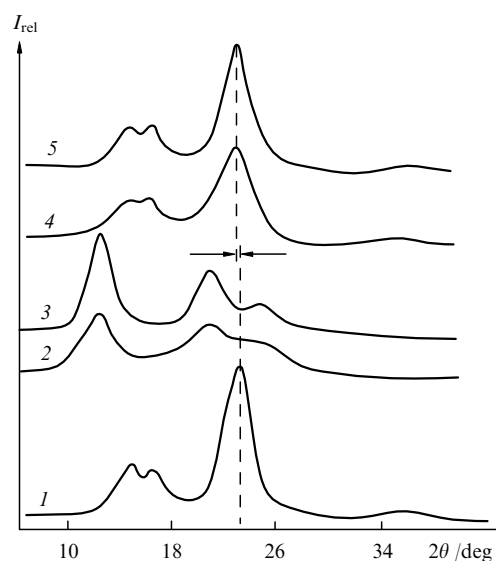


Figure 11. Equatorial diffractograms for the initial flax cellulose (1), highly substituted cellulose nitrite obtained with the aid of N_2O_4 alone (2) and a N_2O_4 –diethyl ether mixture (3), Cel-I regenerated with water from specimens 2 (4) and 3 (5).

native cellulose and that after a cycle of topochemical transformations are not quite equivalent has been confirmed. On the diffractogram of the latter, the (002) reflection is displaced by $\sim 0.4^\circ$ towards smaller diffraction angles (Fig. 11).^{128–130}

The sorption-type KC is also a labile product of the interaction of cellulose with N_2O_4 .^{10, 69, 121, 123} The extremely scanty and contradictory information about its composition and structure is almost fully confined to the data in Refs 29–31, 131, and 132. This compound is formed in the reaction of cellulose with HNO_3 in the monohydrate form. As a rule, the acid concentration of 68 mass %–69 mass % is employed. The azeotropic mixture corresponding to 68.4% HNO_3 is characterised by extremal physical properties⁷⁸ and a weak nitrating activity.^{31, 131, 132} According to Gess,¹³¹ KC is an oxonium compound, being a product of the addition of HNO_3 to the oxygen of the glucoside group of cellulose. The results of calorimetric measurements¹³³ have confirmed this view.

On the basis of the analysis of texture X-ray diffraction patterns and certain assumptions, Andress³⁰ proposed a monoclinic unit cell for KC with the following parameters: $a = 12.20 \text{ \AA}$, $b = 10.28 \text{ \AA}$ (fibre axis), $c = 9.73 \text{ \AA}$, and $\beta = 53^\circ$. Somewhat later Mark¹³² assessed these data as reliable only with regard to the identity period. From the standpoint of the modern concept of the formation of cellulose adducts,^{108, 127} the crystalline phase of KC should be regarded as a result of the insertion and stoichiometric 'fixation' of HNO_3 between the least interlinked (101) planes of the three-dimensional lattice of cellulose. The movement of these planes away from one another along the large ac diagonal (cell projection) is accompanied by a decrease in the angle β without affecting significantly the (10 $\bar{1}$) and (002) planes (Fig. 12). The (101) reflection on the X-ray diffraction pattern of the new phase is displaced towards smaller diffraction angles. Andress identified this reflection as due to the (001) plane, emphasising at the same time the constancy of the (10 $\bar{1}$) and (002) interplanar spacing in the transformation of the Cel-I lattice into the KC lattice.³⁰

The KC lattice is formed in the interaction between cellulose and N_2O_4 under the conditions of the generation of HNO_3 from N_2O_4 directly in the swollen fibre.^{10, 69, 121–123} The reactions of N_2O_4 with cellulose (nitrosation of cellulose) and also with the moisture in cellulose and in the surrounding medium (hydrolysis of N_2O_4) are the sources of the accumulation of HNO_3 . For example, keeping of N_2O_4 -impregnated air-dry cellulose in an atmosphere with a moderate relative humidity (50%–60%) leads

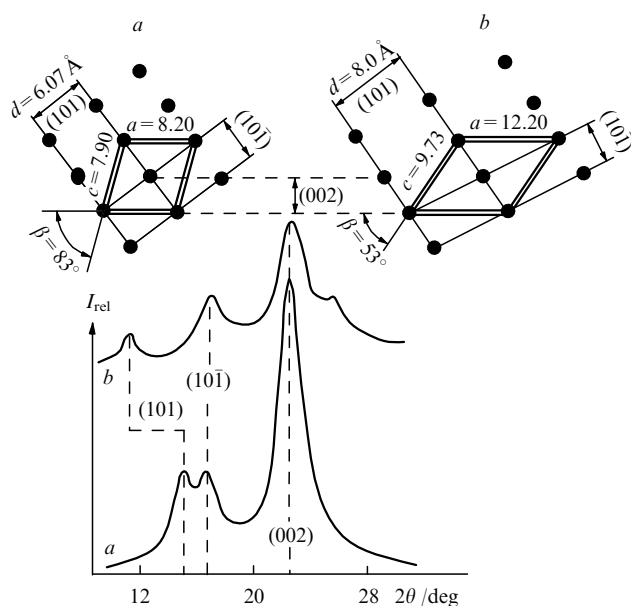


Figure 12. Schematic illustration of the transformation of the Cel-I unit cell (a) into the KC unit cell (b) and the corresponding changes in the diffractogram.

to the formation of KC. After only 15 min of the free evaporation of nitrogen oxides from the swollen fibre, the reflections due to cellulose nitrite vanish from its diffractogram¹²¹ and the angular distribution in the reflections present^{69, 121} corresponds exactly to that indicated by Andress³⁰ for the cellulose adduct with 68.6% HNO_3 . The KC thus obtained is distinguished by an increased crystallinity and the corresponding well resolved X-ray diffraction pattern (Fig. 13). It is formed under the conditions of the decomposition of the cellulose nitrite formed initially, i.e. in a system with a weakened intermolecular interaction and an enhanced segmental mobility of the macromolecules. It is this peculiar 'chemical plasticisation' effect, that most probably creates favourable kinetic preconditions for the formation of the perfect KC crystal lattice.

It has been noted^{128, 129} that the equatorial KC diffractogram changes somewhat with time (Fig. 13). After the specimen has

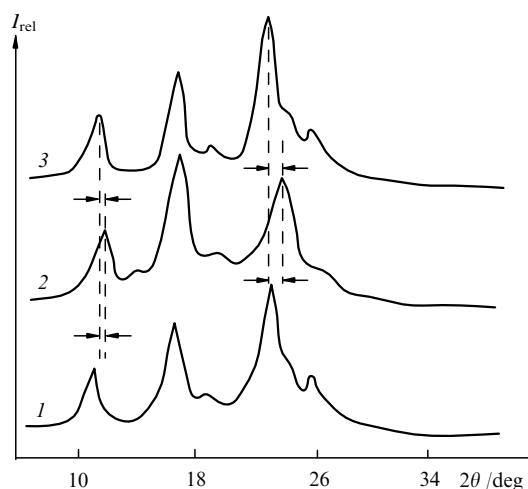


Figure 13. Equatorial diffractograms for KC obtained with the aid of N_2O_4 at a relative humidity of 53%.

(1) initial diffractogram; (2) after keeping specimen 1 under room conditions for 24 h; (3) after additional treatment of specimen 2 with N_2O_4 under previous conditions.

been kept for 20 h under room conditions, the reflections at $2\theta = 11.2^\circ$ and 22.8° are displaced to $2\theta = 12.0^\circ$ and 24.0° , indicating the densification of the crystallites. Judging from the meridional diffractograms,¹²⁸ the identity period remains unchanged (10.3 Å). Additional treatment with N_2O_4 of the specimen having the modified lattice under the previous conditions restores the initial diffractogram and improves somewhat the degree of its resolution. These observations suggest that KC is polymorphic, by analogy with alkaline cellulose.¹²⁷ The inconstancy of the KC crystal structure is apparently due to the change in its composition as a result of the evaporation of 'guest' molecules. According to Mark's data,¹³² the adducts $\text{C}_2\text{H}_{10}\text{O}_5 \cdot \text{HNO}_3$ and $2\text{C}_6\text{H}_{10}\text{O}_5 \cdot \text{HNO}_3$ are characterised by identical diffraction pattern. This is attributed to the presence in the former case of an excess of HNO_3 , sorbed on the surfaces of the crystallites and not involved in the formation of the lattice. Postulating the involvement of partly oxidised cellulose macromolecules in the formation of KC, Urbanski and Zyszczyński³¹ do not reflect the chemical changes in the formula quoted: $2\text{C}_6\text{H}_{10}\text{O}_5 \cdot \text{HNO}_3 \cdot \text{H}_2\text{O}$. Their conclusion that cellulose undergoes preliminary oxidation at the sixth carbon atom conflicts with many evident experimental results.⁹ The specific feature of the structure of KC are still not understood. The possibility of increasing the amount of information derivable from the texture X-ray diffraction pattern of the KC obtained using N_2O_4 makes it possible to hope for a more rigorous quantitative description of the crystal structure of this compound.

On treatment with water, the KC crystallites are always transformed into Cel-II crystallites.^{9, 10, 131, 132} The mechanism and conditions of this transformation are on the whole similar to the usual mercerisation of cellulose.⁷⁷ The degree of the polymorphic transformation of Cel-I into Cel-II via KC reflects a measure of the involvement of the crystallites of the initial material in the adduct formation process.^{9, 10} From the standpoint of permeating capacity, N_2O_4 has considerable advantages over 68%–69% HNO_3 .^{10, 77}

The crystallinity of cellulose nitrite, and that of KC, can be logically regarded as naturally 'inherited' from the lattice of cellulose itself. In view of the lability of these derivatives, the application to them of the familiar artificial crystallisation procedures (for example, heat treatment) does not appear possible. Nevertheless, evidence for the spontaneous formation of the crystalline phases of both cellulose trinitrite^{128, 129, 134} and KC^{123, 134–138} has been obtained in experiments on cellulose known to be amorphous. The high extent of 'amorphousness' of the initial model preparation, isolated from cellulose nitrite solution by special precipitation and regeneration methods,^{139, 140} has been confirmed by the rapid and complete hydrolysability in dilute HCl. The cellulose trinitrite obtained from this preparation crystallised slowly on standing in the nitrosating medium (N_2O_4 –diethyl ether) even at 0°C (Fig. 14). Two weak reflections (instead of one), distinguishing Cel-II trinitrite from Cel-I trinitrite, are gradually outlined on its diffractogram in the range $2\theta = 24–25^\circ$.^{128, 129} A similar difference between diffractograms is characteristic also of Cel-I and Cel-II trinitrites.¹⁴¹ The decomposition of the specimens in cold water leads to Cel-II, while their decomposition by steam affords Cel-IV (Fig. 14). Instances of the formation of Cel-IV in the high-temperature saponification of stable Cel-II esters are known.¹⁴² Thus amorphous cellulose can be converted into Cel-IV via its nitrite ester, an appreciable crystallisation effect being attained. Clearly, there can be no question of this type of ordering effect in chemically unaltered amorphous cellulose using treatment with hot steam for 1 min.

The crystallisation of amorphous cellulose as KG has been observed at room temperature on treatment with 68% HNO_3 and N_2O_4 under the conditions discussed.^{123, 134–138} The use of N_2O_4 leads to an appreciably greater crystallisation effect, as in the experiments with the usual amorphous-crystalline cellulose.^{121, 128, 129} The process is extended in time, but has a distinct X-ray diffraction expression (Fig. 14). The kinetic causes of the

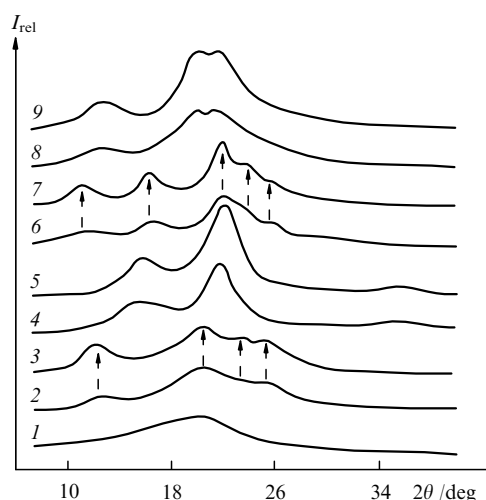


Figure 14. Diffractograms for isotropic specimens.

(1) initial amorphous cellulose; (2) and (3) trinitrite obtained from amorphous cellulose after being kept for 2 h (2) and 21 h (3) in a N_2O_4 –diethyl ether mixture at 0 °C; (4) and (5) Cel-IV regenerated with steam from specimens 2 and 3 respectively; (6) KC obtained from amorphous cellulose (by treatment with 68% HNO_3 for 4 h); (7) KC obtained from amorphous cellulose (by treatment with N_2O_4 for 1 h, relative humidity 55%); (8) and (9) Cel-II regenerated with water from specimens 6 and 7, respectively.

phase transformation are evident. The weakening of the intermolecular interactions by the formation of an adduct and due to other factors^{123, 136} stimulates crystallisation. Hitherto the formation of cellulose adducts (inclusion compounds)^{108, 127} has been traditionally treated regardless of the amorphous regions of the fibre. In relation to KC, first data have been obtained^{123, 134–138} concerning the possibility of the formation of crystallites of these compounds via a mechanism other than that¹²⁷ involving the insertion of ‘guest’ molecules in the finished lattice. Such a lattice is also produced as a result of the self-organisation of the unordered cellulose macromolecules bound to HNO_3 . The crystallinity of KC attained during the self-organisation process is ‘transmitted’ to the Cel-II regenerated from this compound with water (Fig. 14). According to the results of a series of studies,^{9, 123, 136, 138} the amorphous regions also perform a ‘mediating’ function, promoting the penetration of the reagent into the crystallites and the complete formation of a new crystalline phase. The participation of the amorphous regions in the formation of the crystalline phase of the cellulose adducts has been confirmed by the analogous experiments with alkaline cellulose.^{136–138} However, the nonrigorous stoichiometry of the interaction in this system precludes a distinct X-ray diffraction expression of the crystallisation effect of the kind observed in the case of KC.

One of the characteristic features of the heterophase transformation of cellulose on treatment with N_2O_4 into a labile chemical or sorption derivative is the high crystallinity of the final reaction product. A high crystallinity is also characteristic of various polymorphic modifications of cellulose itself, regenerated with water from these labile compounds. The manifestation of this topochemical property has been illustrated^{128, 129} by a series of diffractograms (Fig. 15), reflecting a series of consecutive transformations of cellulose on the same fibrous specimen. If the initial Cel-I specimen is used and its treatment with N_2O_4 under appropriate conditions is alternated with treatment with water, then the following topochemical transformations can be observed on the basis of clear diffraction patterns:

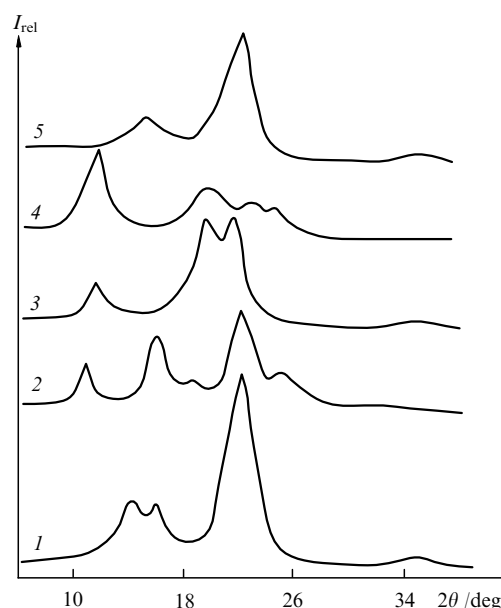
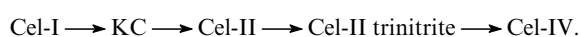


Figure 15. Equatorial diffractograms obtained in succession for flax cellulose (1), Knecht's compound (2), Cel-II (3), Cel-II nitrite (4), and Cel-IV (5).

Conditions in the treatment of the specimen: (1) N_2O_4 , relative humidity 53%; (2) H_2O , 20 °C; (3) N_2O_4 – $(\text{C}_2\text{H}_5)_2\text{O}$; (4) H_2O , 100 °C.

Taking into account the above specific features of the formation of labile derivatives of cellulose and of its polymorphic transformations via these derivatives, one can account for the causes of the amorphisation of cellulose, which is possible under these conditions. The type of polymorphic modification of cellulose regenerated in water from the labile derivative depends on its nature. The formation of each labile compound separately in the interaction of cellulose with liquid N_2O_4 requires particular conditions for the accumulation and distribution of HNO_3 in the system.¹²⁹ The usual conditions in the preliminary treatment,^{10, 101–105, 121} initiating both reaction paths at the intracrystallite level, lead to the regeneration of amorphous cellulose. Judging from the nature of the diffractogram (Fig. 16),^{10, 121, 129} obtained in the stage involving the interaction of cellulose with N_2O_4 , a product of the ‘copolymer type’ is formed in this case. The main bulk of the chain molecules are converted into a mixed

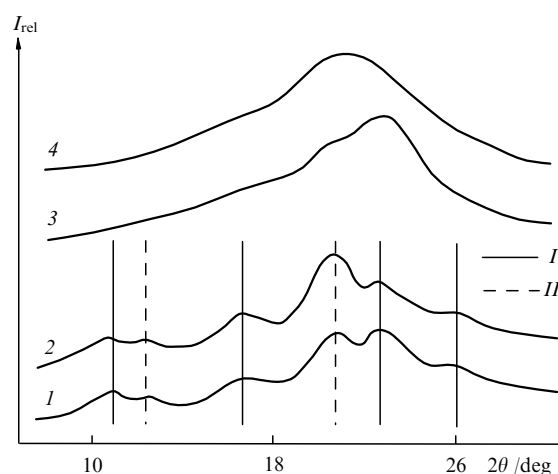


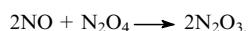
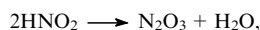
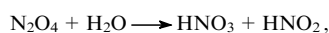
Figure 16. Diffractograms for isotropic flax cellulose specimens swollen in N_2O_4 (1), wood cellulose of the ‘Raycord’ brand (2), and the products of their interaction with water (3, 4). (I) KC; (II) cellulose nitrite.

derivative, losing their regular structure, which actually leads to a general disorganisation of the system (intense diffuse scattering on the diffractograms).

The uniform sequences of cellulose nitrite and KC units present in individual microvolumes form crystalline inclusions, the fraction of which is small (weak reflections against the background of diffuse scattering). The balance between cellulose nitrite and KC is unstable, the system tending to be wholly transformed into KC under the influence of small amounts of water, which actually occurs when it is absorbed from air with a humidity of 50%–60%. Only the most unstable component (cellulose nitrite) decomposes under these conditions, stimulating the formation and crystallisation of KC. On rapid decomposition by an excess of water of both labile components simultaneously, the structural imperfection of the mixed cellulose derivative is 'transmitted' to the cellulose regenerated from it (Fig. 16). The elements of order in the cellulose decrystallised in this way are contributed by crystallite formations comprising cellulose nitrite and KC, which are transformed by the action of water into Cel-I and Cel-II respectively. Weak signs of crystallite scattering by these cellulose modifications are frequently manifested on the diffractograms of the amorphised specimens, which are on the whole diffuse.^{101, 103, 114} A convincing demonstration of their presence in the amorphous 'matrix' follows from the diffractograms of the fraction of amorphised preparations which is difficult to hydrolyse.^{105, 114} The degree of decrystallisation of cellulose increases appreciably when an undried organic solvent with a high affinity for nitrogen oxides and HNO₃, for example, diethyl ether or acetic acid, is used instead of water to wash the treated fibre.^{10, 100, 101, 126} These regeneration conditions hinder the transformation of the crystalline cellulose nitrite and KC formations into the corresponding crystalline modifications of cellulose.

Brief contact (15–20 s) between air-dry cellulose and liquid N₂O₄ is favourable for amorphisation.¹⁰ A short reaction time promotes the attainment of a disordered state of the system, limiting structure formation in the rapidly formed labile products. For example, the intracrystallite swelling of cellulose in 68%–69% HNO₃ is known to be completed after ~2 min,^{9, 136} but an increase in the crystallinity of KC is observed over a period of many hours of contact between the fibre and the acid.¹³⁶

The degree of amorphisation of cellulose depends on its moisture content and on the amount of moisture absorbed from the air by the fibre swollen in N₂O₄. It has been noted¹⁰⁵ that, in order to obtain X-ray-amorphous cellulose, the fibre interacting with N₂O₄ should contain at least 5%–7% of water, i.e. should be air-dry. The formation of KC participating in the amorphisation process is not alone in being coupled with the moisture content factor. For a high moisture content in cellulose or a high humidity of air, the process can also be influenced by the formation of N₂O₃ in accordance with the following equations:



A mixture of N₂O₄ and 3%–10% of N₂O₃ is capable of effecting the transition of cellulose to the gel state or a solution.¹³ The shrinkage and conversion into a gel-like formation of a bundle of cellulose fibres on wetting both with purified N₂O₄ under the conditions of a high relative humidity of air (92%) with and a mixture of the above nitrogen oxides (for a humidity of 53%), obtained by passing NO into cooled N₂O₄, has been noted.¹²⁹ According to an X-ray photodiffractogram, the chemically unaltered cellulose regenerated from the gel with water or alcohol is an isotropic amorphous material.¹²⁹ It is remarkable that such treatment of the fibre with N₂O₄ under the conditions of moderate humidity (50%–60%) leads to the formation of the KC crystal lattice, from which textured Cel-II with a high degree of

crystallinity can be readily regenerated with water.^{10, 129} It is logical to assume the possibility of the local manifestation of the homogenisation effect for an increased moisture content in cellulose. Outwardly this may be undetectable owing to the presence of an excess of N₂O₄.

Cellulose dried beforehand is resistant to amorphisation by N₂O₄.^{105, 126} After contact with N₂O₄ and washing with water, its structure corresponds to the Cel-I modification, as for the material generated with water from cellulose nitrite (Fig. 11). However, under conditions inducing the rapid nitrosation of air-dry cellulose^{69, 129} the transformations of the 'dehydrated' cellulose on treatment with liquid N₂O₄ are extremely unusual. An idea about their dynamics is provided by the diffractograms presented in Fig. 17, which were obtained in the following readily reproducible experiment. A specimen comprising dried (105 °C, 2 h) flax cellulose fibres was treated with liquid N₂O₄ under conditions promoting esterification^{69, 129} and was rapidly isolated from the external medium. This was followed by the repeated recording of X-ray diffractograms in the range of angles 8–25 °C at an equatorial scanning rate of 2 deg min⁻¹. Thus the recording of one diffractogram after another (Fig. 17) reflects the course of the structural changes in the fibre throughout approximately 1.2 h since the start of the recording. It follows from then that the rapid intracrystallite interaction of the 'dry' cellulose with N₂O₄ is characterised by a surprisingly high stoichiometry. The new unstable crystalline phase formed in the course of several minutes is distinguished by an individual angular distribution of the diffractogram reflections and by a higher degree of order than in cellulose itself, its trinitrite, or KC. According to the subsequent diffractograms, the crystal lattice of the initial phase approaches that characteristic of cellulose trinitrite as a result of continuous transformations. In the analogous experiments with an air-dry fibre, the diffractogram of cellulose trinitrite is obtained immediately (Fig. 11).^{69, 129}

It may be postulated that a small amount of sorbed water stimulates the nitrosation of cellulose as a result of the ionisation of N₂O₄, whilst in the case of 'dehydrated' cellulose the process is extended over a period of time and it is possible to observe the diffractograms of the transition state adducts. At the same time the complex and varied nature of the interaction of cellulose with pure N₂O₄ does not rule out also other causes of the above transformations. The decisive influence of the moisture content factor on the transformations in the given system is evident, but has not been established in all its manifestations. Without taking into account this influence, seemingly identical reaction conditions may lead to different results.^{114, 138}

The effectiveness of combining N₂O₄ with glacial acetic acid in the preparation of amorphous cellulose has already been noted.^{12, 77, 110, 111} In the presence of carboxylic acids, the nitrosation of cellulose is not complicated by side reactions. According to series of X-ray diffraction features, the swelling of cellulose nitrite in carboxylic acids, (ranging from acetic to valeric) is an intracrystallite process.^{77, 80, 124} The diffractograms of the preparations swollen in the esterifying mixture show, together with the reflections due to cellulose nitrite, an average-angle reflection ($2\theta = 6-7^\circ$), which reflects the appearance in the lattice of a fairly extended (~13 Å) periodicity (Fig. 18). As a result of the displacement of the carboxylic acid from the esterified preparations by absolute diethyl ether, the above periodicity is eliminated, the swelling of the fibre diminishes appreciably, and the reflections due to the crystalline phase of cellulose trinitrite intensify. Such periodicity is also manifested when dry cellulose nitrite, prepared with the aid of diethyl ether, is acted upon by a carboxylic acid. With increase in the length of the hydrocarbon component of the acid molecule, the new interference shifts into the region of smaller angles.^{77, 88} With increase in the degree of swelling of the preparation, its intensity increases synchronously with the degeneration of the (220) and (440) reflections due to cellulose nitrite ($2\theta = 12.4^\circ$ and 24.8°) and then, as the preparation decomposes, it diminishes to zero. The variation of the intensity of the reflection

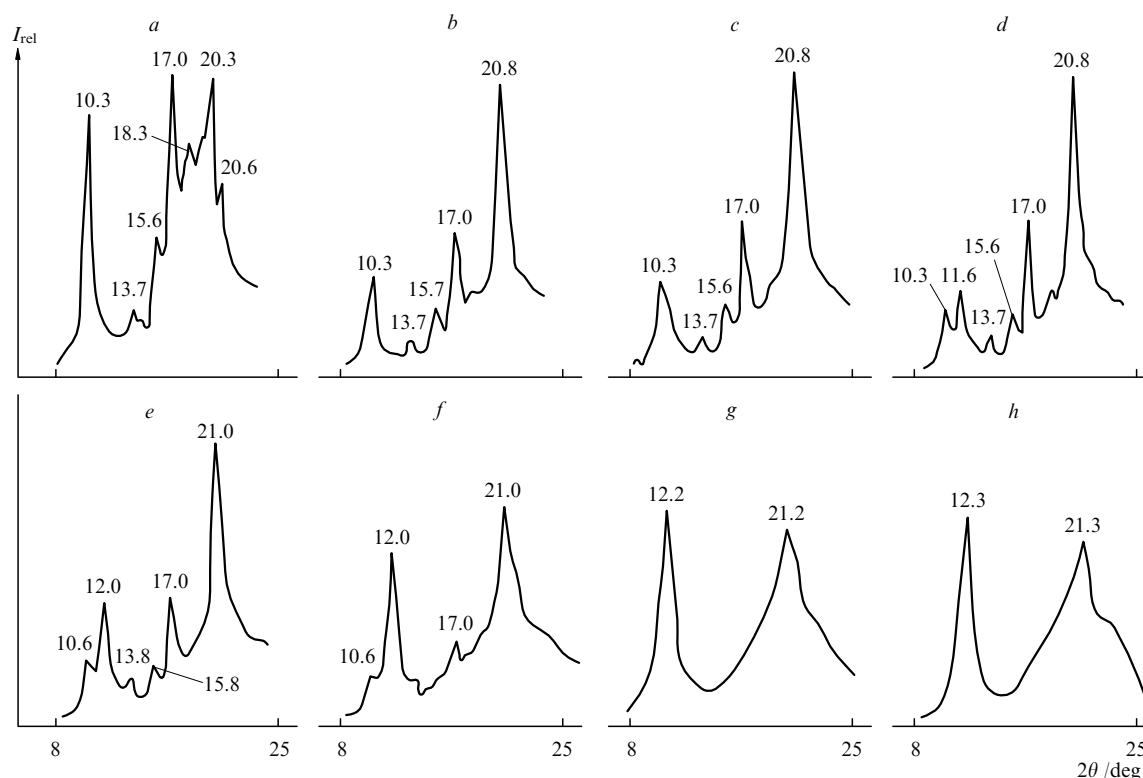


Figure 17. Dynamics of the structural rearrangement in the interaction of 'dry' cellulose with N_2O_4 .

Time elapsed from the start of the experiment to the completion of the recording of the corresponding diffractogram (min): (a) 9; (b) 18; (c) 27; (d) 36; (e) 45; (f) 54; (g) 62; (h) 72.

due to cellulose nitrite also passes through an extremum at $2\theta = 20.8^\circ$, the reflection shifting towards larger diffraction angles and becoming diffuse.⁸⁰ There is every reason to suppose that cellulose nitrite swells as a result of the insertion of the acid into the lattice between the (220) planes, the new periodicity appearing as a result of the planes 'moving apart'. Comparison of the increment in the (220) interplanar spacing with the sizes of the carboxylic acid molecules shows that this hypothesis is tenable.

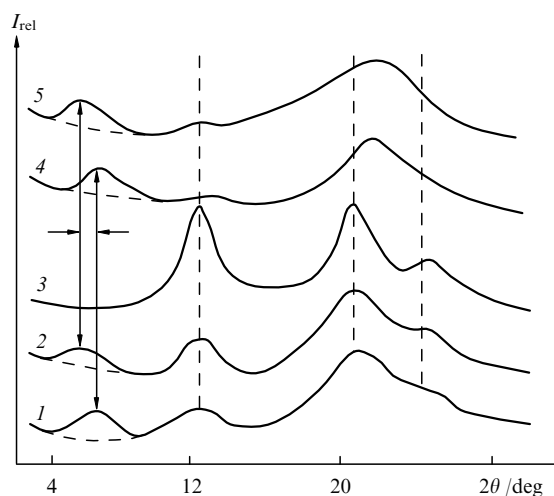


Figure 18. Diffractograms of the products of the interaction of cellulose nitrite with carboxylic acids.

Specimen: (1) specimen swollen in the N_2O_4 -acetic acid esterifying mixture; (2) specimen swollen in the N_2O_4 -butyric acid esterifying mixture; (3) specimen 1 after washing with absolute diethyl ether; (4) and (5) specimens swollen in acetic and butyric acids respectively.

The regeneration of cellulose during the washing of the esterified and swollen fibre with glacial acetic acid is actually its regeneration from the additive compound of cellulose nitrite with the acid under the influence of the moisture absorbed from air.⁸⁰ As a hygroscopic substance, glacial acetic acid functions as a moisture conductor, ensuring its equal access to the amorphous and crystalline regions of the swollen fibre. Denitrosation proceeds slowly, in accordance with the statistical principle, introducing a structural disorganisation into the system. An appreciable decrystallisation effect can be attained by not allowing the decomposition of cellulose nitrite in acetic acid to go to completion, the process being stopped by washing with water, as a result of which structurally nonordered cellulose is rapidly and fully recovered from its partly substituted labile ester with an irregular structure. The direct action of water on the esterified preparation rules out the isolation of X-ray-amorphous cellulose.⁷⁷ Complete denitrosation in acetic acid gives rise to the greatest decrystallisation effect. This process, limited by the amount of sorbed moisture, can be greatly extended in time. Gert et al.¹¹¹ determined the degree of swelling of the fibre in acetic acid after the displacement of the latter with N_2O_4 from the product of the treatment of cellulose with a mixture of the above reagents, assuming that the swollen material comprises chemically unaltered amorphous cellulose. The value obtained (300%) exceeds the value of WRC (250%) established by the same gravimetric method after the displacement of acetic acid with water. The swelling of chemically unaltered cellulose in acetic acid cannot exceed its swelling in water. For the initial cellulose, the degrees of swelling are respectively 11% and 37%.^{12, 111} Evidently the swollen specimen employed for the analysis consisted of partly substituted cellulose nitrite, the decomposition of which was completed in the course of the drying of the sample.

The degree of decrystallisation of cellulose is very sensitive to the degree of swelling in the nitrosating mixture, i.e. to the mixture composition, temperature, and the reaction time.^{12, 77} Fig. 9 illustrates the effectiveness of the employment of different com-

positions of the acetic acid–N₂O₄ mixture for the decrystallisation of cellulose during 20 min interaction at the liquid modulus value of 20 ml g⁻¹. In all cases, identical conditions were maintained in the denitrosation reaction, which was stopped by the action of water. As can be seen, the use of mixture of acetic acid with 18 vol. %–20 vol. % of N₂O₄ (5 mol of acetic acid per mole N₂O₄) at 30 °C makes it possible to amorphise cellulose almost entirely. This composition actually induces the highest degree of swelling, of the cellulose nitrite formed, since it exhibits a fairly high nitrosating activity at 30 °C (Fig. 8) At the same time, the composition includes an appreciable amount of free acid (the molar ratio in the acetic acid–N₂O₄ complex is 2 : 1; melting point 2 °C).⁷⁴ It is not fortuitous that the combination of N₂O₄ with a cellulose nitrite solvent (methyl acetate) is used in such proportion to dissolve cellulose.^{1,27} The change in this composition in any direction decreases sharply the decrystallisation effect, giving rise to an extremum in the variation under discussion (Fig. 19). The same behaviour is manifested also as a lower temperature of the 20 min treatment of cellulose with acetic acid–N₂O₄ mixtures of different composition. The weakening of the nitrosating activity leads in this case to a smaller degree of decrystallisation of cellulose. A fairly rigorous correlation between the crystallinity index and the WRC of the preparations indicates that the measurements made are correct.

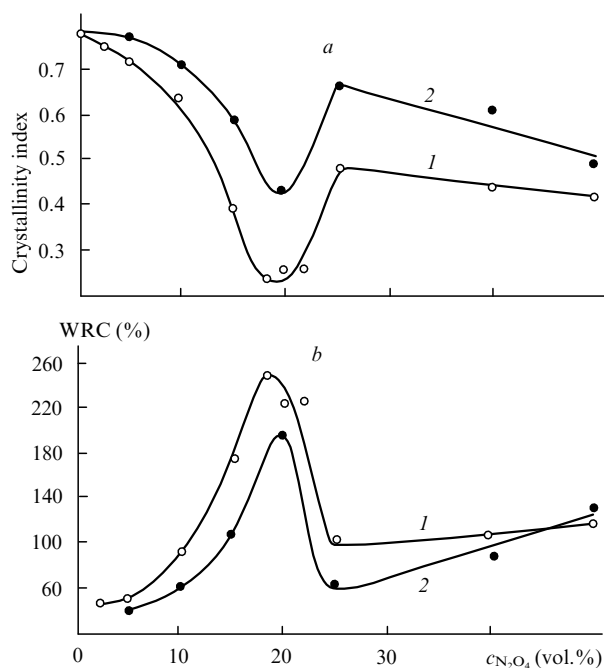


Figure 19. Variation of the crystallinity index (a) and the water retaining capacity (WRC) (b) of cotton cellulose as a result of treatment with N₂O₄–acetic acid mixtures of different composition.

Treatment conditions: 20 min; liquid modulus 20 ml g⁻¹, temperature 30 °C (1) and 25 °C (2).

Thus the use of the acetic acid–N₂O₄ system for the preparation of amorphous cellulose is based on the specific features of the swelling and decomposition of cellulose nitrite in acetic acid.

V. Examples of the applied importance of labile nitrogen-containing polysaccharide derivatives

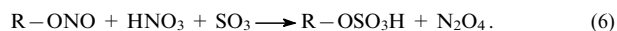
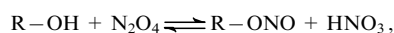
In this section, we shall confine ourselves to the discussion of certain rational approaches to the preparation of materials of practical importance, based on polysaccharides with participation of their labile derivatives. This methodology is based on the

principle of the combined use of several functions of the reaction medium and of the unstable polymeric compound formed in it.

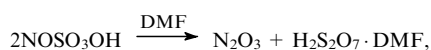
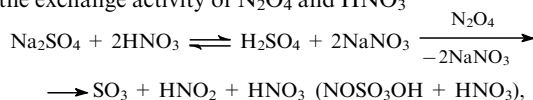
A good example is the homogeneous conversion of polysaccharides into sulfates in the DMF–N₂O₄ system by ‘generated reactants’ method.^{143–146} The sulfates of accessible polysaccharides (cellulose, dextran, mannan, chitosan) possess a biological activity, like the expensive and difficult to isolate heparin, chondroitin sulfate, etc.¹⁴⁷ The most effective procedure for the uniform conversion of polysaccharides into sulfates is the homogeneous transesterification of the nitrites with the highly toxic and corrosive SO₃ in the DMF–N₂O₄ system.^{16, 17, 50} It has been suggested^{143–146} that the usual sodium and potassium salts of the acids H₂S_nO_{2n+1} (n = 1, 2) or H₂S_nO_{3n+1} (n = 1–3), which are themselves incapable of esterifying polyhydroxypolymers and function as ‘stored’ forms of SO₃, generating the latter on being acted upon by the reaction medium, be used for the formation of sulfates in the above system. Apart from homogenising the system as a result of the formation of the nitrite ester, the presence of N₂O₄ ensures the sulfating activity of the potential source of SO₃.

Reactants stimulating sulfate formation can act as oxidants, or can participate in exchange processes, or can combine the oxidising and exchange functions depending on the type of sulfur-containing compound employed. The first role is assumed when SO₂ is converted into the sulfating complex between SO₃ and the solvent.¹⁴⁸ The role of N₂O₄ is not restricted solely to the nitrosation of the polysaccharide and the generation of SO₃. The equilibrium degree of substitution as regards sulfo-groups depends on the ratio N₂O₄/SO₃, it diminishes with increase in the ratio.

Thus, apart from the known instability of sulfate esters in relation to acid media, account must be taken also of the desulfating activity of N₂O₄, i.e. the existence in the reaction systems of equilibrium between the sulfate and nitrite ester substituents in the polysaccharide:

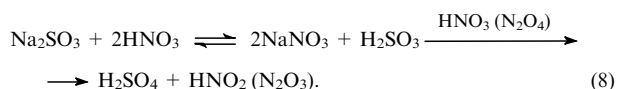


When salts of the acids H₂S_nO_{3n+1} are used as the source of sulfur, the reactive sulfating agent is generated (*in situ*) as a result of the exchange activity of N₂O₄ and HNO₃



The SO₃ evolved from the salts shifts equilibrium (6) towards the formation of the sulfate ester. By virtue of the homogeneity and reversibility of the process, the displacement of nitrite by sulfate ester groups takes place uniformly. The cellulose sulfates obtained dissolve fully in water even for DC = 0.2, which is not attained under any other known sulfate formation conditions.

A mixed type of the activating influence of N₂O₄ and HNO₃ is manifested in relation to salts of the acids H₂S_nO_{2n+1}:



It follows from Eqns (7) and (8) that, when salts with tetravalent sulfur are used, both exchange and oxidation reactions take place. The latter lead to heating of the system and the acceleration of the reaction. Salts with hexavalent sulfur are preferable because in this case the equilibrium is established slowly without heating, which creates ‘mild’ synthesis conditions and prevents degradative transformations of the macromolecules. The overall synthesis time is reduced as a result of the combination of the stages involving the dissolution of the starting material and its

conversion into a sulfate on simultaneous introduction of the polymer and the salt into the DMF–N₂O₄ mixture. The mannan and dextran sulfates synthesised in this way exhibit a distinct anticoagulant activity for the corresponding degrees of substitution but are not toxic even in large doses (2–5 g kg⁻¹).¹⁴⁹

Partial nitrosation of cellulose in acetic acid may be of practical interest as an effective preactivation method in the preparation of cellulose acetates.^{12, 113, 126, 150} The high reactivity of cellulose nitrite in the homogeneous transesterification reactions with acetylating agents is known.^{8, 50} The proposed activation procedure reduces to brief treatment of cellulose with a solution of N₂O₄ in glacial acetic acid and subsequent displacement of the free nitrogen oxides from the fibre by the same acid.^{112, 113, 126, 150} The traditional industrial schemes for the activation of cellulose are also based on the treatment of the fibre with acetic acid.^{107, 151} The addition of small amounts of N₂O₄ (5 vol. %) does not induce excessive swelling of the fibre, so that the activation process is achieved simply and rapidly, achieving nevertheless an appreciable increase in reactivity (Table 6). After such activation, even mercerised cellulose, characterised by a low reactivity in acetylation, is acetylated almost wholly.¹⁰⁷ By carrying out the reaction up to the appearance of a 'clear field' in acetone, it is possible to obtain partially substituted cellulose acetates (DS = 2.12–2.26; DP = 420–590) soluble in acetone, dioxane, DMF, acetic acid, and other solvents.^{126, 150} The properties of these products are similar to those of the secondary cellulose acetates obtained via a two-stage scheme: full acetylation of cellulose — partial homogeneous hydrolysis. The known methods for the direct synthesis of such materials^{151, 152} are based on the acetylation of cellulose in the presence of large amounts of H₂SO₄ (15%–25% of the mass of cellulose) and on the reaction being carried out in dioxane. The same 'chemical activation' principle (in the present instance, by conversion into a sulfate) is used. Such methods are more complex. The mixed esterification of cellulose leads to the homogenisation of the reaction mixture in early stages of the reaction and to uniformity of the substitution by acetyl groups, as a result of which the partly substituted cellulose acetate dissolves in organic solvents. In order to isolate cellulose acetate in a pure form and impart thermal stability to it,¹⁵³ a special operation involving the saponification of the sulfate ester groups is carried out. Analogous materials are prepared from partly nitrosated cellulose by means of an acetylating mixture having the usual composition and additional stabilisation procedures are not required.

In contrast to alkaline cellulose, Knecht's compound has not found a practical application. Nevertheless, when cellulose is

processed in acid media, for example, for the preparation of its powdered forms, one can employ successfully the same properties of KC as those of alkaline cellulose. These are primarily the ability to induce the polymorphic transformation of cellulose and to serve as a reactive additive 'matrix' for chemical modification in accordance with a principle similar to that underlying the xanthogenation of alkaline cellulose.

It has been suggested^{33, 154–157} that chemically unchanged microcrystalline Cel-II (MCCel-II) be obtained from native cellulose in accordance with a purely acid scheme, where HNO₃ performs the functions of both 'mercerising' and hydrolysing agents. After the interaction of cellulose with 68%–69% HNO₃, the liquid is squeezed out of the swollen fibre and the strong acid remaining in it is diluted with water to a concentration of 5%–15%, which ensures the selective hydrolytic cleavage of the fibrous system on subsequent heating. As a result of dilution, Cel-II is regenerated from KC and is then hydrolysed with the weak HNO₃ solution formed until the attainment of the 'limiting DP'. The simplicity and rationality of this scheme, eliminating the traditional mercerisation of cellulose with a solution of alkali, are evident. Furthermore, MCCel-II is obtained by the acid scheme with a lower crystallinity than the product formed by the alkaline-acid scheme.¹⁵⁶

The reverse sequence of operations also leads to the 'mercerisation' effect, i.e. treatment of the MCCel-I obtained beforehand with 68%–69% HNO₃ and then water. In this variant, there is the attractive possibility of attaining the virtually complete amorphisation of microcrystalline cellulose by increasing the duration of the reaction with 68%–69% HNO₃ to 2–4 h.^{32, 156, 158, 159} The main cause of decrystallisation is the uniform partial nitration of the microcrystalline cellulose. While possessing a low nitrating activity, 68%–69% HNO₃ is nevertheless capable of esterifying cellulose to a slight extent (DC = 0.1–0.3) under the conditions of prolonged contact. The intracrystalline character of the swelling (the formation of KC) ensures the uniformity of the substitution by nitro-groups. The product isolated by treatment with water is weakly nitrated powdered decrystallised cellulose (PDC).

Powdered celluloses obtained by the above procedures are distinguished by high specific surfaces and sorption activities. (Table 7). In terms of the retention of water and the sorption of iodine and a dye, they are greatly superior to the microcrystalline cellulose prepared in the traditional way. It has been noted that HNO₃ in the form of the monohydrate, induces (like N₂O₄) the appearance of microcracks in the cellulose fibre. Their branched network has been observed on fibre cross-sections⁷⁷ and on the lateral surfaces of PDC particles¹⁵⁸ under a scanning electron microscope. The microcracks and the low crystallinity of the materials are responsible for the manifestation of strong sorption properties. The familiar bleaching activity of HNO₃ and nitrogen oxides^{7, 8} is expressed by the high degree of whiteness of the powdered form of cellulose obtained with their aid.

The possibility of the effective employment of KC in the preparation of monocarboxycellulose, in particular its powdered forms, has been established.^{34, 156, 160} The preactivation of native cellulose with 68%–69% HNO₃ (the formation of KC) makes it possible to increase greatly the rate and uniformity of the subsequent oxidation in the same acid at a somewhat lower concentration (55%–60%). The concentration of HNO₃ is reduced in the oxidation stage in order to weaken its nitrating activity. The oxidation reaction is initiated by the generation of nitrogen oxides from HNO₃. For this purpose, sodium nitrite is introduced into the system or the reaction temperature is increased. By virtue of preactivation, the fraction of the material oxidised at a high, virtually constant rate increases by a factor of 3–5,¹⁶⁰ which makes it possible to obtain rapidly uniformly oxidised cellulose, containing up to 17 mass % of carboxy-groups (the oxidation of the sixth carbon atom in all the GPU corresponds to 25.57 mass % of COOH groups). The bound nitrogen content in the specimens is 0.28 mass %–0.46 mass %.¹⁶⁰

At elevated temperatures, the cellulose oxidation and hydrolytic decomposition reactions coincide in time. Preactivation

Table 6. Results of acetylation by the methylene chloride method of cotton cellulose activated at 20 °C with acetic acid, or the N₂O₄–acetic acid mixture followed by displacement with glacial acetic acid.

Acitvation conditions	Reaction time until attainment of clear field /min	DS of cellulose acetate	DP of cellulose acetate
Initial cellulose — native			
1 h, 80% AA	180	2.85	740
20 min, N ₂ O ₄ –AA mixture (20 : 80)	7	2.86	400
5 min, N ₂ O ₄ –AA mixture (5 : 95)	30	2.92	650
Initial cellulose — mercerised			
1 h, 80% AA	180 (no homogenisation)	1.62	
5 min, N ₂ O ₄ –AA mixture (5 : 95)	50	2.90	

Note. Acetylating mixture: acetic anhydride–acetic acid–methylene chloride (30 : 10 : 60 vol. %), catalyst — perchloric acid (~1% of mass of cellulose), liquid modulus 10 ml g⁻¹, temperature 26 °C.

Table 7. Characteristics of powdered forms of cellulose.

Specimen	WRC ^a	Sorption/mg g ⁻¹		DP	Degree of whiteness (%)
		I ₂	Congo Red		
MCCel-I, FND brand (Filtrak Company)	43	19.0	288	180	95
MCCel-I, LT Brand (Lachema Company)	49	57.0	414	180	90
Sulfate MCCel-I (hydrolysis with 2.5 N HNO ₃)	46 (48)	18.0	247	170	95
Sulfate MCCel-II, obtained by the alkaline-acid scheme	70 (117)	30.5		50	96
Sulfate MCCel-II, obtained by the acid scheme	81 (122)	151.0	550	50	98
PDC (2.2% N), obtained from sulfate MCCel-I	108 (182)	312.0		150	96
PDC (1.3% N), obtained from MCCel-I, LT brand (Lachema Company)	95 (156)	238.0	640	150	94

^a The number in brackets characterises the water-washed final product before drying.

accelerates sharply both reactions. The hydrolysis of cellulose itself stimulates the oxidation reaction, because its products have a reductive function, promoting the formation of nitrogen oxides in the system. It is important to balance these reactions in such a way that the degree of hydrolysis does not affect negatively the yield of powdered oxidised cellulose.¹⁶⁰

Oxidation of preliminarily dispersed cellulose, for example, microcrystalline cellulose, in accordance with this scheme, should be carried out at normal or reduced temperatures, initiating the reaction by adding N₂O₄ or sodium nitrite. There are virtually no mass losses in this case. By virtue of preactivation, the reaction from its very beginning, takes place also in the crystallites themselves and not only on their surfaces, so that the final products are characterised by a low degree of structural order even for a relatively low degree of oxidation.¹⁶⁰

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Metal ions in unusual and unstable oxidation states in aqueous solutions: preparation and properties

B G Ershov

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Abstract. The properties of short-lived metal atoms and ions in unusual oxidation states in aqueous solutions, characterised by the presence of one electron in the outer *s* or *p* orbitals (the $d^{10}s^1$ and $d^{10}s^2p^1$ configurations respectively), are discussed. The results of studies on such ions by pulse radiolysis with rapid optical detection and by the matrix isolation method in frozen aqueous solutions are presented. The nature of the dependences of fundamental characteristics of metal atoms and ions (optical transition energies, the electronic structures of various complexes, the oxidation-reduction potentials, etc.) on their positions in the Periodic System are analysed. The bibliography includes 93 references.

I. Introduction

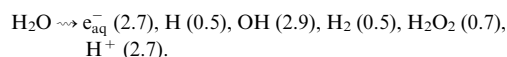
Atoms and ions in unusual and unstable oxidation states are formed at intermediate stages of oxidation-reduction reactions occurring with participation of polyvalent metals. Despite the short time of their existence, their important role in the occurrence and effectiveness of many processes in chemistry and biology is evident. The existence of metal ions in unusual oxidation states has been postulated, and in a number of instances has been confirmed experimentally, in connection with the justification of the multistage nature of electrochemical reactions and the explanation of catalytic steps with participation of metals and the characteristic features of the mechanisms of many other oxidation-reduction processes. The above species can be obtained by pulse radiolysis in aqueous solutions in one-electron reduction or oxidation reactions of metal ions and they are investigated with the aid of optical or coulometric detection. Procedures involving the radiation-induced generation of metal ions in unusual oxidation states in inert matrices at a low temperature with subsequent study by stationary optical and EPR spectroscopic methods are also widely employed.

During the last thirty years investigators have studied in fair detail, employing the above approaches, the properties of many metal ions in unusual valence forms in aqueous media. The results of studies available by 1981 were analysed in our previous review.¹ New data, which make it possible to reach definite conclusions about the regularities in the variation of fundamental properties of metals in unusual oxidation states as a function of their position in the Periodic System, have now accumulated. The study of the chemistry of such elements has become possible as a result of advances, in the first place in radiation chemistry, and also the development of the method of pulse radiolysis.²

This review is devoted to a discussion of the properties of metals in unusual and unstable oxidation states in aqueous solutions and to the establishment of the regularities in their manifestation as a function of the position of the element in the Periodic System. The review is concerned predominantly with metal ions having one electron in the outer *s* and *p* orbitals, *i.e.* with the $d^{10}s^1$ and $d^{10}s^2p^1$ electronic configurations (copper, silver, gold, zinc, cadmium, mercury, gallium, indium, thallium, tin, lead, antimony, and bismuth).

II. Radiation-chemical preparation of atoms and ions of metals in unusual oxidation states

The radiation-chemical reduction or oxidation of metal ions in aqueous solutions is effected by the ionic and radical species which arise on decomposition of water as a result of its interaction with ionising radiation. In a general form, the latter process can be described by the following equation:

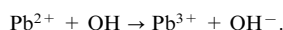
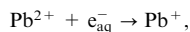


The primary radiation-chemical yields of the species in the solution volume per 100 eV of the absorbed energy for light types of radiation (γ -rays or accelerated electrons), the linear energy transfer for which is small, are presented in brackets. The hydrated electron e_{aq}^- and the hydrogen atom H formed have high reduction potentials (-2.7 and -2.3 V respectively), while the hydroxyl radical OH has a high oxidising capacity (2.9 V). For this reason, when the ratio of the potentials in their interaction with metal ions satisfies the requirement that the free energy of the system diminishes, one-electron reduction or oxidation reactions take place. For example, both processes take place in the case of Pb^{2+} ions.

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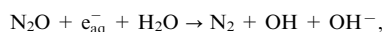
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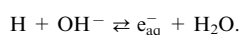
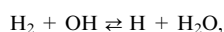
Under these conditions, ions in unusual and unstable oxidation states are produced. They have the electronic configurations $d^{10}s^1$ and $d^{10}s^2p^1$ for Pb^{3+} and Pb^+ respectively.

As a rule investigators used for the study of metal ions in unusual oxidation states solutions in which predominantly reducing or oxidising species may be obtained. We shall illustrate this in relation to OH radicals. On order to obtain OH radicals, a solution is saturated with nitrous oxide. The limiting concentration of the gas under normal conditions in a neutral solution is ~ 0.05 M. As a result of the reaction

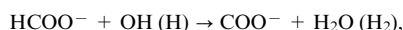
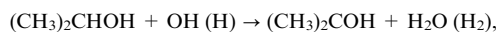


the rate constant for which is 9×10^9 litre $\text{mol}^{-1} \text{s}^{-1}$,³ virtually only hydroxyl radicals are formed in aqueous solution.

Hydrated electrons alone may be obtained only in alkaline solutions ($\text{pH} > 12$), saturated with molecular hydrogen, via the following reactions:



The pK for the second equilibrium is 9.6, *i.e.* the hydrogen atom is a weak acid. However, the rate constant for the reaction of molecular hydrogen with the hydroxyl radical is insufficiently high (3.7×10^7 litre $\text{mol}^{-1} \text{s}^{-1}$). In order to increase the rate of reaction, it is necessary to employ high hydrogen pressures, which is difficult to achieve experimentally. Furthermore, hydrogen atoms are transformed into hydrated electrons only in a highly alkaline medium, where many metal ions are precipitated in the form of hydroxides. Therefore, in order to create a reducing medium, use is made of aqueous solutions to which organic compounds — alcohols or organic acid salts — are added as hydroxyl radical and hydrogen atom scavengers. For example, when isopropyl alcohol or a formic acid salt is added, the reactions



generate only reducing species — hydrated electrons and organic radicals — on exposure to ionising radiation. The oxidation-reduction potentials (E^0) of certain organic radicals, most frequently employed in radiation-chemical studies, have been determined from measured equilibrium constants for the reactions involving the reduction of thallium ions by such radicals ($E^0 = -1.94$ V). The following values were obtained:^{4,5}

Parameter	CO_2^-	$(\text{CH}_3)_2\text{COH}$	CH_3CHOH	CH_2OH
$-E^0/\text{V}$	1.9	1.39	1.25	1.18

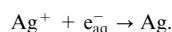
The presence of one electron in the outer s or p orbital of the metal atom or ion is responsible for an exceptionally high reactivity. Such species may be compared with radicals, which also have an unpaired electron. The lifetimes of metal ions belonging to the s and p blocks and having unusual oxidation states in aqueous solutions are determined by kinetic factors. The rate constants for their dimerisation or disproportionation are as a rule $10^9 - 10^{10}$ litre $\text{mol}^{-1} \text{s}^{-1}$. The preparation and study of such species in aqueous solutions are therefore associated with the employment of methods which make it possible to detect fast processes, in the first place pulse radiolysis with optical detection of short-lived products,^{1,2,6} as well as low-temperature radiolysis [usually in glassy aqueous solutions at the temperature of liquid nitrogen (77 K)]. The method involving the matrix isolation of the highly reactive species formed under these conditions makes it possible to investigate them by stationary electron spin resonance (ESR) or optical spectroscopic methods.

III. Atoms and ions of metals in unusual oxidation states in aqueous solutions

1. Copper, silver, and gold atoms

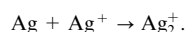
The radiation-chemical reduction of silver has been most thoroughly investigated.⁷⁻⁹ We shall deal in somewhat greater detail with the methodological features of the experiments on the preparation and study of silver atoms in aqueous solutions, because they are fairly applicable also to other metals.

In a dilute aqueous solution of a silver salt (AgClO_4 at a concentration of $10^{-5} - 10^{-3}$ M is usually employed), containing alcohol or HCOONa as the hydroxyl radical scavenger, an intense optical absorption due to the hydrated electron with $\lambda_{\text{max}} = 720$ nm is observed immediately after the application of a short electron pulse (with a nano- or micro-second duration). The decrease in this absorption is accompanied by the appearance of a new absorption band with $\lambda = 360$ nm. The rates of decrease in the intensity of the first absorption and of increase in that of the second are proportional to the concentration of the silver ions present in the solution. When the solutions are saturated with nitrous oxide, the hydrated electrons are transformed into OH radicals. The appearance of a band with $\lambda = 360$ nm is not then observed. The observed changes in the optical absorption spectra are probably caused by the reaction



This hypothesis has been confirmed by the observation of the effect of ionic strength on the rate of reaction which is of the kind expected for the interaction of species bearing unlike charges. The conductivity of the aqueous solution increases under these conditions owing to the formation of a proton.

The rate constant for the reduction of silver ions by electrons has been determined from the analysis of the kinetics of the decrease in the optical absorption due to the hydrated electron, which is described by pseudo-first-order kinetics. The rate constant was found to be 4.8×10^{10} litre $\text{mol}^{-1} \text{s}^{-1}$.⁹ In the measurement of the optical spectrum of atomic silver, it is essential to bear in mind that its absorption bands overlap with those of the hydrated electron and the organic radical, formed immediately after the application of the accelerated electron pulse and disappearing in subsequent reactions, and also with the bands due to a new species — the Ag_2^+ cluster generated in the reaction



Bearing this in mind, Ershov *et al.*⁹ exposed a deaerated AgClO_4 solution (1×10^{-4} M) containing 0.1 M isopropyl alcohol to a short 15 ns electron pulse, the absorption spectrum being measured after 0.1 μs . During the time elapsed, only 36% of the hydrated electrons were trapped by the silver ions. Allowance for the absorption due to the remaining hydrated electrons and $(\text{CH}_3)_2\text{COH}$ radicals, as well as the silver ions consumed as a result of the reduction made it possible to calculate the absorption spectrum due to Ag^0 atoms in the aqueous solution. The spectrum consists of a broad band with $\lambda = 360$ nm; the extinction coefficient (ε) is 1.6×10^4 mol litre cm^{-1} , whilst the band width at the half the height is 0.91 eV (Fig. 1).

The preparation of copper atoms in unusual oxidation states is complicated compared with the preparation of silver atoms by the fact that in aqueous solutions copper in the stable state has a degree of oxidation of +2. Solutions of copper salts in the +1 oxidation state are unstable and are readily oxidised to the +2 state. In order to increase their stability, ligands capable of forming copper(I) complexes are added to the solution. Sukhov *et al.*¹⁰ used neutral aqueous deaerated CuCl solutions ($1 \times 10^{-4} - 3 \times 10^{-3}$ M) containing 2 M NaCl. Under these conditions, copper(I) ions exist predominantly as the complexes CuCl_3^{2-} (80%) and CuCl_2^- (20%). It was observed that, after irradiation with accelerated electrons for 15 ns, the decrease in the absorption due to hydrated electrons at 720 nm is accompanied by the appearance of an absorption band with $\lambda = 380$ nm.

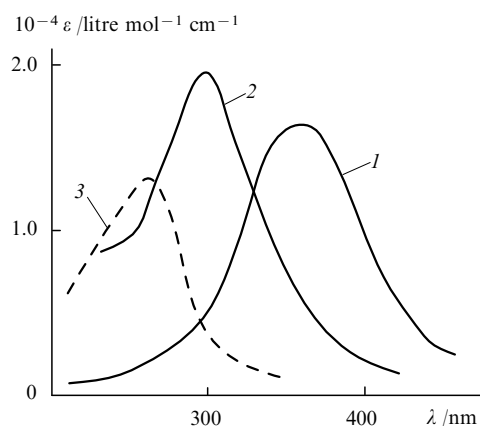
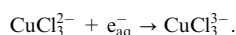


Figure 1. Optical absorption spectra of the atoms and ions of metals with the $d^{10}s^2p^1$ electronic configuration in water. (1) Ag^0 ; (2) Cd^+ ; (3) In^{2+} .

However, in contrast to the analogous processes described above for silver ions, the increase in the intensity of the band with $\lambda = 380$ nm is slower than the decrease in the intensity characterising the disappearance of hydrated electrons. Furthermore, the rate of destruction of the latter was proportional to the concentration of the copper(I) ions present in the solution. However, this did not affect the appearance of the new band. The kinetics of the disappearance of e_{aq}^- in CuCl solutions are described satisfactorily by a first-order equation with an effective rate constant which depends linearly on the concentration of the dissolved salt. All these features suggest that the electrons are destroyed in a reaction of the type

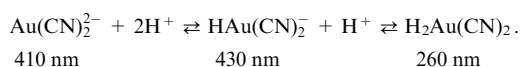


The calculated effective rate constant for the interaction of e_{aq}^- with monovalent copper(I) chloride complexes is $2.7 \times 10^{10} \text{ litre mol}^{-1} \text{ s}^{-1}$.¹⁰ We may note that the hydroxyl radicals formed oxidised copper(I) to copper(II). Analysis of the characteristic features of the kinetics of the appearance of the absorption band with $\lambda = 380$ nm suggests that it is due to the copper atoms formed in the decomposition of the unstable chloride complex:



The kinetics of the formation of copper atoms are described by a first-order equation with an effective rate constant of $4.7 \times 10^7 \text{ s}^{-1}$.¹⁰

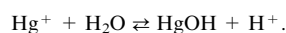
About thirty years ago, it was established¹¹ that the product of the reduction of the $\text{Au}(\text{CN})_2^-$ ion by hydrogen atoms in an aqueous acid solution has an absorption band with a maximum at 260 nm, while the product of the reduction by hydrated electrons in a neutral medium is characterised by a band with a maximum at 410 nm. It has been suggested that the above absorption bands are associated with the adducts $\text{HAu}(\text{CN})_2^-$ and $[\text{Au}(\text{CN})_2] \dots e_{\text{aq}}^-$. In a later publication,¹² it was shown that reduction with formation of a product in three equilibrium forms depending on the pH, each of which is characterised by different optical absorption bands, does indeed take place in both cases.



The $\text{p}K$ is 5.9 and ~ 5.2 for the first and second equilibria respectively. It was also established that all three complexes decompose with formation of gold atoms, which have a low-intensity absorption band with $\lambda_{\text{max}} < 260$ nm. The reaction is first-order with rate constants of 6.7×10^3 and $5.3 \times 10^4 \text{ s}^{-1}$ for $\text{Au}(\text{CN})_2^{2-}$ and $\text{H}_2\text{Au}(\text{CN})_2$ respectively.

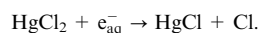
2. Zn^+ , Cd^+ , and Hg^+ ions

The formation of monovalent zinc and cadmium ions as a result of reduction by hydrated electrons of the divalent metal ions in neutral aqueous solutions was observed more than twenty years ago.^{13–15} It was found that the univalent ions have intense absorption bands at 300 nm. The results of the latest more careful experiments¹⁶ suggest that the Zn^+ ion does indeed have an absorption band with a maximum at 310 nm, while the absorption band due to the Cd^+ ion is probably at 295 nm (Fig. 1). The formation of Hg^+ ions was observed in the reduction of divalent mercury by hydrogen atoms in aqueous media.^{17,18} A feature distinguishing this species from those examined above with the $d^{10}s^1$ electronic configuration is the presence of two absorption bands with maxima at 225 and 255 nm,¹⁷ which is apparently a consequence of the splitting of the p level. The Hg^+ ion hydrolyses in solution:



The logarithm of the equilibrium constant of this reaction is 5.1.¹⁸ According to the study quoted, the hydroxo-complex HgOH is characterised by two absorption bands — at 233 and 265 nm. The presence of an additional band with a maximum at 360 nm has also been established.¹⁹ We may note an interesting feature of the formation of the Hg_2^{2+} ion by the dimerisation of Hg^+ ions. The process is complex and takes place in two consecutive reactions: in the first, the disproportionation of Hg^+ ions results in the formation of a mercury atom, while in the second the atom reacts with a Hg^{2+} ion, affording Hg_2^{2+} .

It has been shown²⁰ that HgCl_2 molecules interact with hydrated electrons:



The rate constant for this reaction ($2.7 \times 10^{10} \text{ litre mol}^{-1} \text{ s}^{-1}$) is high.

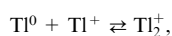
The HgCl molecules are characterised by two optical absorption bands — at 245 and 330 nm. These molecules disappear, giving rise to Hg_2Cl_2 . The formation of HgCl molecules in the reduction of HgCl_2 has been demonstrated by electron paramagnetic resonance.²¹ After γ -irradiation of frozen aqueous sulfuric acid solutions of this salt at 77 K, a signal due to the HgCl molecule is observed. Its quartet hyperfine structure is due to the interaction of the unpaired electron with the ^{35}Cl and ^{37}Cl magnetic nuclei, the nuclear spins of which are identical and equal to $3/2$, while the magnetic moments are similar. In concentrated hydrochloric acid solutions (8 M), mercury is present in the form of the complex HgCl and the reduction of the mercury ion is not accompanied by the splitting off of chloride ions.²¹ The formation of the HgBr^{22} and HgI^{23} molecules has been detected by pulse radiolysis in the reduction of the corresponding divalent mercury salts in aqueous solutions.

3. Ga^{2+} , In^{2+} , and Tl^{2+} ions and In and Tl atoms

The Ga^{3+} and In^{3+} ions are vigorously hydrolysed in aqueous solutions. It has been established that these ions and their hydrolysed forms are virtually not reduced by hydrogen atoms and the formation of the Ga^{2+} and In^{2+} ions, occurring in aqueous and neutral solutions, is a result of the interaction only with hydrated electrons.^{24–26} The absorption band maxima of the Ga^{2+} and In^{2+} ions are at 268 and 263 nm respectively. The absorption spectrum of the indium aquo-complex in the $+2$ oxidation state is presented in Fig 1. The Tl^{2+} ion has been obtained in a strongly acid medium on reduction of trivalent thallium by hydrogen atoms.²⁷ Its absorption, the maximum of which occurs at wavelengths shorter than 225 nm, has been recorded. We may note that, together with the main absorption band, an additional shoulder appears for the hydroxo-complexes of divalent gallium²⁵ and thallium^{27–30} — at 300 nm for the first complex and 360 nm for the second.

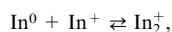
The Tl^+ ion is stable in aqueous solutions. The oxidation-reduction potential of the Tl^+/Tl^0 couple is -1.94 V, which implies

the possibility of its reduction by both hydrated electrons and hydrogen atoms in aqueous solutions. It has been shown³¹ that this does indeed take place. Fairly concentrated salt solutions and long electron pulses (2 μ s) were used in the experiments. As a consequence of the high rate of the reaction



the equilibrium constant of which is 2.3×10^3 litre mol⁻¹, the optical absorption due to thallium atoms was hardly observed owing to the intense absorption due to the Tl_2^+ species formed (a band with a maximum at 420 nm). Ershov *et al.*³² refined the characteristics of the absorption spectrum of thallium atoms. A low concentration of Tl^+ ions (1×10^{-4} M) was used for this purpose, the solution containing also isopropyl alcohol as a hydroxyl radical scavenger. The spectrum was recorded 0.7 μ s after the application of 15 ns or 0.5 μ s electron pulses. Under these conditions, the equilibrium in the last reaction is displaced to the left. It was established that the absorption by Tl^0 (Fig. 2) includes two bands — at 450 nm ($\epsilon = 5 \times 10^3$ litre mol⁻¹ s⁻¹) and at 260 nm ($\epsilon = 9 \times 10^3$ litre mol⁻¹ s⁻¹).

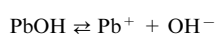
The In^+ ion is unstable in aqueous solutions and is readily oxidised, forming In^{3+} ions. The calculated reduction potential of indium atoms in aqueous solution proved to be -2.3 V.³³ It is identical with the potential of hydrogen atoms. This means that In^+ ions could be reduced only by hydrated electrons. Aqueous InBr solutions were used in the above study.³³ In the presence of bromide ions, univalent indium becomes more stable. It has been established that the indium atoms arising immediately after the application of a 15 ns electron pulse are characterised by absorption bands with maxima at 500 nm and at a wavelength shorter than 300 nm. After a time, the intensities of the above bands fall and new bands appear at 310 and 460 nm. The rate of appearance of the latter increased with increase in the salt concentration in solution. The above changes were induced by the reaction



the equilibrium constant of which is approximately 5×10^2 litre mol⁻¹. We may recall that, in contrast to the metal atoms and ions examined above, having the $d^{10}s^1$ configuration, indium and thallium atoms are characterised by the $d^{10}s^2p^1$ electronic configuration.

4. Pb(I) and Pb(III) ions

Lead aquo-complexes in the +1 and +3 oxidation states were obtained when Pb^{2+} ions were reduced by hydrated electrons and oxidised by hydroxyl radicals in aqueous, neutral, and alkaline aqueous solutions. The Pb^+ ion is formed on pulse radiolysis in neutral or weakly acid Pb^{2+} solutions.^{34–36} Its absorption spectrum is presented in Fig. 2. The ion has a $d^{10}s^2p^1$ outer electron shell and gives rise to a low-intensity absorption band at 320 nm ($\epsilon = 2.5 \times 10^3$ litre mol⁻¹ cm⁻¹). Divalent lead ions are readily hydrolysed in aqueous solutions. At pH 6 they already exist in the PbOH^+ form. The formation of the Pb^{3+} aquo-complex may therefore be expected only for acid aqueous solutions. Indeed the above ion is formed on oxidation of Pb^{2+} by hydroxyl radicals at pH < 4 in aqueous solutions saturated with N_2O .³⁷ Its absorption band, with a maximum at $\lambda < 220$ nm, extends into the UV region. At pH ~ 4 an additional weak shoulder is formed at 330 nm and is due to the hydroxo-complex PbOH . The pK value for the hydrolytic reaction



is 4.0. At pH > 6, an additional shoulder is also observed at 360 nm with the absorption band in the UV region.³⁸ The electrical conductivity of the solution does not change under these conditions, which suggests the following reaction:

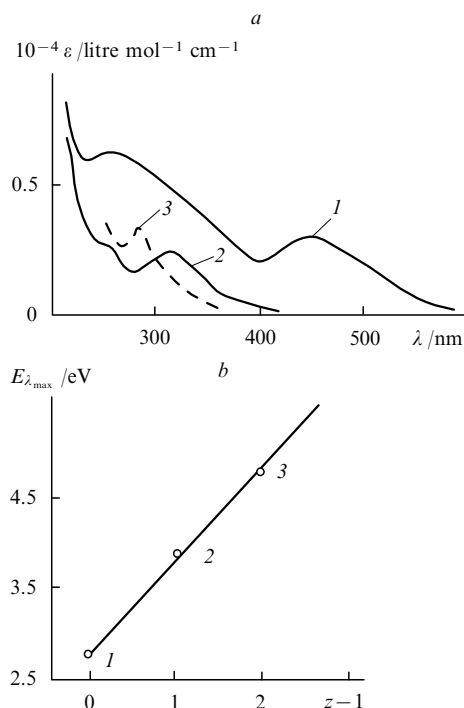
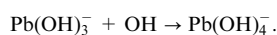
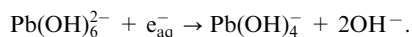


Figure 2. Optical absorption spectra of the atoms and ions of metals with the $d^{10}s^2p^1$ electronic configuration in water (a) and the dependence of $E_{\lambda_{\max}}$ on the charge (b). (1) Tl^0 (2) Pb^+ ; (3) Bi^{2+} .

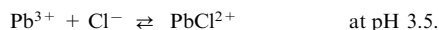
At pH 11.4, divalent lead forms the hydroxo-complex $\text{Pb}(\text{OH})_3^-$. The $\text{Pb}(\text{OH})_4^-$ species probably arises in its interaction with the OH radical:



Its absorption spectrum is characterised by a narrow band at 280 nm and a broader band at ~ 360 nm. The same species appears in the reduction of tetravalent lead in a highly alkaline solution (pH 13) by the reaction



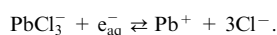
The complex PbCl_2^+ has been obtained in the oxidation of Pb^{2+} ions (5×10^{-4} M) by hydroxyl radicals in neutral and acid aqueous solutions saturated with nitrous oxide and containing chloride ions ($> 5 \times 10^{-2}$ M).³⁹ The increase in the charge on the lead ion and the decrease in its radius compared with the Pb^{2+} ion led to the formation of a monochloride complex in the reactions



The pK values for the above equilibria are 1.2 and 2.6 respectively.

The optical absorption of the above complex includes four bands with $\lambda_{\max} = 276, 320, 380$, and 485 nm, while the extinction coefficients are respectively 6.0×10^4 , 3.1×10^4 , 3.2×10^4 , and 1.2×10^4 litre mol⁻¹ cm⁻¹.

On the other hand, the PbCl molecule did not arise on reduction of lead(II) chloride complexes by hydrated electrons even at a chloride ion concentration of 0.1 M. The following reaction occurred under these conditions;



Only in the presence of NaCl in the solution (~ 2 M) was the formation of PbCl observed (main absorption band at wavelengths less than 280 nm, additional bands at 300 and 390 nm). The instability constant of this complex (pK_i) was estimated as approximately -0.3 .³⁹

5. Bi(II) and Bi(IV) ions

Since bismuth is vigorously hydrolysed in aqueous solutions, concentrated perchloric solutions (up to 5 M) are used for its preparation in the initial Bi^{3+} form. Under these conditions, the hydrogen atoms formed after the application of an electron pulse reduce the Bi^{3+} ions to Bi^{2+} (single absorption band with a maximum at 285 nm).⁴⁰ No evidence for the possibility of the oxidation of Bi^{3+} by hydroxyl radicals and the formation thereby of Bi^{4+} ions was found. This reaction probably does not occur at all owing to the high oxidation potential of Bi^{4+} . Indeed, an estimate of this potential yields ~ 3.5 V, which is significantly higher than the potential of the OH radical (2.9 V).

Ionic Bi(II) and Bi(IV) chloride complexes have been obtained by pulse irradiation of concentrated aqueous hydrochloric acid solutions.⁴¹ The absorption due to the Bi(II) ion is characterised by two bands with maxima at 350 and 460 nm and that due to the Bi(IV) ion is characterised by bands at 270 and 370 nm.

IV. Atoms and ions of metals in unusual oxidation states in frozen aqueous solutions

The method for the preparation of metal ions in unusual oxidation states in frozen aqueous solutions is based essentially on the same reactions involving reduction by electrons, formed on ionisation of the medium, and oxidation by the hydroxyl radicals, arising in ion–molecule reactions of the positively charged H_2O^+ parent ions (see, for example, Ershov and coworkers^{42,43}). Concentrated aqueous solutions of a wide variety of electrolytes, for example, perchloric, sulfuric, hydrochloric, and other acids and their salts or alcohols, to which the metal salts investigated are added, are used for these purposes. On rapid freezing of such solutions in liquid nitrogen, transparent glasses, retaining to the maximum extent the structure of the liquid aqueous media, are formed. During exposure to ionising radiation (usually ^{60}Co γ -radiation), the metal ions are reduced by thermalised mobile electrons. The metal atoms or ions formed are stable indefinitely at 77 K. The oxidation reactions of the metals occur on raising the temperature to ~ 150 K. At this temperature, the hydroxyl radicals localised in intermolecular traps become mobile. Many atoms and ions of metals in unusual oxidation states have been obtained and investigated in this way.^{44–56}

It was found that the optical characteristics of the atoms and ions of metals with $d^{10}s^1$ or $d^{10}s^2p^1$ outer electron shells in aqueous solutions at room temperature and at the temperature of liquid nitrogen do not differ significantly. Only a 10–20 nm hypsochromic shift and some narrowing of the band are observed. The most significant results were obtained in the study of the ESR spectra of the metal atoms and ions in frozen aqueous media. Indeed, by means of the ESR method one can not only demonstrate the very fact that the atoms and ions in unusual oxidation states are formed but the structure of the paramagnetic centre, the nature of the environment, and the nature of the distribution of the unpaired electron can also be determined.

Metals usually have several isotopes, some of which may carry a nuclear spin. The paramagnetic ions formed on addition of a single electron to the outer s orbital are therefore characterised by the presence of two types of signals. The first are due to isotopes without nuclear spin and are represented in the ESR spectra by singlets in the region of the g -factor of the free electron. The second are due to isotopes carrying a nuclear spin and their ESR spectra are characterised by the presence of a hyperfine structure (HFS). Light elements (copper and silver) differ from others by the fact that the HFS constants of the ESR signals are small but sufficient for observation in the usual microwave spectrometer (magnetic field up to 300–1000 mT). For virtually all other elements, the HFS constants are so large that their resonance frequencies exceed the UHF field frequency employed in the ESR

spectrometer. Only certain components of the HFS of the paramagnetic atom or ion are therefore observed. Fig. 3 presents the ESR spectra for the Ga^{2+} and Pb^{3+} ions. The HFS constants were calculated from the positions of the high-field components of the signals by the Breit–Rabi equation.⁵⁷ Table 1 presents the characteristics of the ESR spectra for a series of paramagnetic metallic species having an unpaired electron in the outer s shell. Evidently, the g -factor exhibits a negative deviation (Δg) relative to the g -factor of the free electron, which is 2.0023. A negative deviation of the g -factor is characteristic of paramagnetic centres with an excess electron. Furthermore, one may note that Δg increases in absolute magnitude along the subgroup and diminishes along one Period with increase in the atomic number of the element. In the former cases, the charge on the paramagnetic species is constant under these conditions, but the mass of the nucleus of the element increases (compare, for example, the equal-charge series, Zn^+ , Cd^+ , Hg^+), while in the latter case the paramagnetic species have the same electronic structure within the limits of the Period, but their charge increases under these conditions (compare the isoelectronic series Ag , Cd^+ , Ga^{2+} , Sn^{3+}). The ratio $A_{\text{iso}}/A_{\text{iso}}^0$, which defines the density of the s state on the metal nucleus, increases within the limits of the equal-charge series of paramagnetic species with increase in the number of the Period. On the other hand, it diminishes within the limits of the isoelectronic series with increase in the charge on the ion.

Table 1. Characteristics of the ESR spectra of the atoms and ions of metals in the electronic state $^2S_{1/2}$ in a frozen aqueous solution at 77 K.^{58–62}

Atom, ion	g -Factor	$A_{\text{iso}}/\text{mT}^a$	$A_{\text{iso}}^0/\text{mT}^b$	$A_{\text{iso}}/A_{\text{iso}}^0$
$^{63}\text{Cu}^0$			2094	
$^{67}\text{Zn}^+$			813	
$^{69}\text{Ga}^{2+}$		2260	5034	0.449
$^{77}\text{Ge}^{3+}$			1077	
$^{109}\text{Ag}^0$	1.9814	580	705	0.773
$^{111}\text{Cd}^+$	1.9896	3250	5137	0.633
$^{113}\text{In}^{2+}$			8139	
$^{117}\text{Sn}^{3+}$	1.9950	6825	15935	0.428
$^{197}\text{Au}^0$			1089	
$^{199}\text{Hg}^0$	1.9818	11350	14453	0.780
$^{203}\text{Tl}^{2+}$		43210	62622	0.690
$^{207}\text{Pb}^{3+}$	1.9920	16000	27796	0.575

^a A_{iso} is the experimental isotropic HFS constant for the metal atom or ion in aqueous solution. ^b $A_{\text{iso}}/A_{\text{iso}}^0$ is the isotropic HFS constant for the atom or ion in the free state.

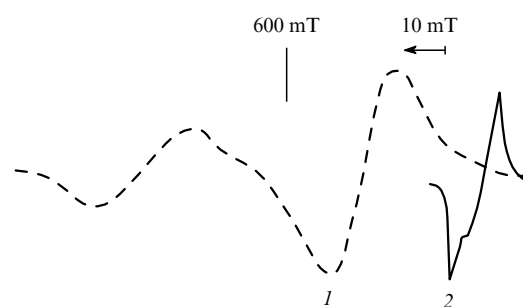


Figure 3. ESR spectra of Ga^{2+} ions at 77 K (1) and Pb^{3+} ions at 150 K (2) in a γ -irradiated HClO_4 solution (6 M). Salt concentration: (1) 0.25 M $\text{Ga}(\text{ClO}_4)_3$; (2) 0.1 M $\text{Pb}(\text{ClO}_4)_2$.

V. Regularities in the variation of electronic properties

In the preparation and study of the properties of metals in unusual oxidation states, characterised by the presence of a single electron in the s or p orbitals, investigators always showed the greatest interest in the aquo-complexes of such metals. This is because the aquo-complexes are in fact most common and have been thoroughly investigated. The regularities in the variation of the fundamental properties of the above metals within the Periods and Groups of the Periodic System have been discovered.^{51, 54–56, 63, 64} We shall deal with some of them. Metals in unusual oxidation states are extremely unstable and exist for a short time, so that the methods for their investigation are limited with the consequent limitation of the available information about their properties. These are in the first place the characteristics of their optical absorption and ESR spectra and the properties of their electronic structures as well as the oxidation-reduction potentials which follow from them.

1. Aquo-complexes

The absorption by the atoms and ions of metals with the $d^{10}s^1$ electronic configuration in an aqueous solution in the state of an aquo-complex is characterised by a single intense UV absorption band. The position of the band undergoes a smooth hypsochromic shift in an isoelectronic series of metals with increase in the charge on the species, as can be seen for the Ag^0 , Cd^+ , In^{2+} series (Fig. 1). We may note that the absorption band of the Sn^{3+} ion, the next member of the above isoelectronic series, is at ~ 215 nm in a frozen aqueous solution at 77 K,⁵⁴ i.e. the tendency for the absorption to be displaced into the UV region with increase in the charge on the ion is continued. Furthermore, the energies of the optical transitions at the absorption band maxima ($E_{\lambda_{\text{max}}}$) increase linearly with increase in z (Fig. 4). In the subgroups, the energies increase with increase in the number of the Period. These regularities, discovered at an early stage of the study of the properties of metals,^{51, 54–56} served as a basis for the prediction of the expected values of $E_{\lambda_{\text{max}}}$ for a series of atoms and ions which at that time had not yet been obtained. Thus the positions of the absorption bands were predicted and later determined experimentally for copper and gold atoms, Pb^{3+} ions, etc.

The optical absorption of the aquo-complexes of metals in the $^2S_{1/2}$ state is due to the $2a_{1g} \rightarrow 2t_{1u}$ transition. This transition can be regarded to a large extent as the transfer of an unpaired electron from the atomic orbital of the central metal ion to the mixed np , $2s$ and $2p$ orbital. The first optical transition in the same metal atoms and ions in the gas phase corresponds to the $S \rightarrow P$ transition. This entails the splitting of the level as a consequence of spin–orbit coupling. Thus in the case of silver atoms the energies correspond-

ing to the $P_{1/2}$ and $P_{3/2}$ levels in the gas phase are respectively 338 and 328 nm. As mentioned above, in water a broad band with a maximum at 360 nm corresponds to silver atoms. This means that, on passing to an aqueous solution, the absorption band undergoes a ‘red’ shift and becomes significantly broader. For this reason, if the splitting due to spin–orbit coupling is not very marked, it is not observed. The differences between the energies of the $P_{1/2}$ and $P_{3/2}$ levels for the Ge^{3+} , Sn^{3+} , and Pb^{3+} ions in the gas phase are 0.346, 0.807, and 2.611 eV respectively.⁶⁵ If one bears in mind that the values of $E_{\lambda_{\text{max}}}$ for atoms and ions in the $^2S_{1/2}$ electronic state in aqueous solutions are in the range from 3 to 6 eV, one may conclude that the splitting of the energy levels may significantly complicate the structure of the bands in the spectra of the aquo-complexes. For elements of the Fourth and Fifth Periods, the above effect most probably leads to the broadening of the absorption bands, while in the case of the Sixth Period the splitting may prove to be considerable. Indeed, two absorption bands have been observed for Hg^+ , at 225 and 255 nm,^{17, 18} which is probably a consequence of the splitting of the p level.

The first optical transition in the aquo-complex corresponds to intracomplex oxidation. The validity of this conclusion is confirmed by the linear correlation between $E_{\lambda_{\text{max}}}$ and the $s^1 \rightarrow p^1$ excitation energies of the ions in the gas phase ($E_{s \rightarrow p}$) (Fig. 5). On the other hand, such correlation between $E_{\lambda_{\text{max}}}$ and the energy of the $d^{10}s^1 \rightarrow d^9s^2$ transition in the gas phase is not observed, which indicates that the optical transition in the aquo-complex is mainly due to the $s^1 \rightarrow p^1$ excitation.⁶³

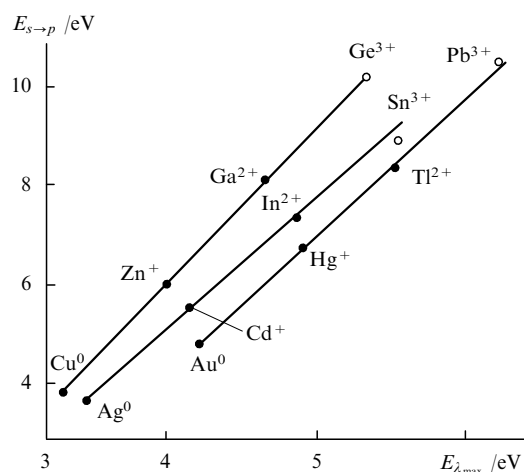


Figure 5. Dependence of $E_{s \rightarrow p}$ for the metal ion in the gas phase on $E_{\lambda_{\text{max}}}$ for the ion in the form of an aquo-complex.

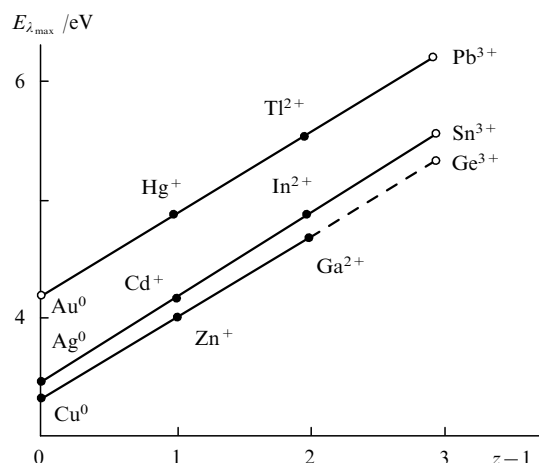


Figure 4. Dependence of $E_{\lambda_{\text{max}}}$ on the charge of the metal ion.

Analysis of spectroscopic data for the gas phase demonstrates the existence of the fundamental linear dependence of $E_{\lambda_{\text{max}}}$ on z of the type established for an aqueous medium.⁶³ The above relation has been justified theoretically⁶⁴ and equations relating the energies of the $s \rightarrow p$ transitions for hydrogen-like ions with a filled d shell to their charge have been derived. The approach is based on the familiar dependence of the energy term for a hydrogen-like ion on the charge. It is described by the Balmer formula, supplemented by relativistic corrections and the relations between the mass and the extent of spin–orbit coupling. Ultimately the following equation, relating the change of the electronic transition energy (expressed in rydbergs) for a hydrogen-like ion to its charge was obtained:

$$E_{ns \rightarrow np} = \frac{2K_n}{n^2} z + az + c, \quad (1)$$

where n is the number of the electron shell and the quantities K_n , a , and c are determined by the shielding constants for the ions and

are found numerically from the dependences of their ionisation potentials in the gas phase on the charge z . For an isoelectronic series of ions, K_n is constant. Fig. 6 illustrates the dependences of the $s \rightarrow p$ transition energies for ions in the gas phase and in aqueous solution on z . They are linear and are described satisfactorily by Eqn (1). There is a slight deviation only for the first elements of the isoelectronic series, namely for copper, silver, and gold atoms. This is probably due to a certain degree of mixing of the s and d electronic states of these atoms. The constants a and c for an aqueous medium are the same as for the gas phase, but the quantities K_n differ significantly (Table 2). The intercept produced by the extrapolation of lines 1 and 2 on the ordinate axis is the same for the gas phase and aqueous solution. The intercept is determined by the constant c in Eqn (1). The physical significance of the constant is that of the energy of the $s \rightarrow p$ transition for an ion with $z = 0$.

Table 2. The coefficients K_n , a , and c of Eqn (1) for isoelectronic ions of the elements in the Fourth, Fifth, and Sixth Periods.

Period	K_n (gas phase)	K_n (aqueous phase)	a	c
4	0.862	0.221	0.035	0.165
5	0.994	0.318	0.031	0.188
6	1.311	0.312	0.042	0.234

Using the simple linear dependence of the $s \rightarrow p$ transition energy on the charge for a series of isoelectronic ions in the $^2S_{1/2}$ electronic states, it is possible to calculate by Eqn (1) or determine graphically (Fig. 6) any fundamental characteristics for ions which have not been obtained in this electronic state in the gas phase (Table 3). The energies of the optical transitions can be determined similarly also for ions in aqueous media. However, the existence of a whole series of these (for example, the As^{4+} , Sb^{4+} , Bi^{4+} , and other highly charged cations of the succeeding subgroup) is impossible because their oxidation potentials are higher than that of the hydroxyl radical.

Table 3. The values of $E_{s \rightarrow p}$ for a series of elements in the Fourth, Fifth, and Sixth Periods in the electronic state $^2S_{1/2}$.

z	Fourth		Fifth		Sixth	
	I ^a	II ^b	I ^a	II ^b	I ^a	II ^b
5	—	—	—	—	Po	12.5
6	Br	15.6	I	13.1	At	14.1
7	Kr	17.4	Xe	14.7	Rn	15.8

^a Element. ^b Energy /eV.

Experimental data on the properties of metal ions having the $d^{10}s^2p^1$ electronic configuration are limited and are in essence confined to the In^0 , Tl^0 , Pb^+ , and Bi^{2+} species. Nevertheless, it is possible to analyse the structure and positions of the optical absorption bands for the isoelectronic series of the above Sixth Period metal ions. Their optical absorption spectra and the dependence of $E_{\lambda_{\max}}$ on the ionic charge (Fig. 2) show that the absorption band on the long-wavelength side shifts to the UV region in the Tl^0 , Pb^+ , Bi^{2+} series, while $E_{\lambda_{\max}}$ increases linearly at the same time with increase in the ionic charge. For equally charged metal atoms in one subgroup (indium and thallium), a hypsochromic shift of the absorption band with increase in the number of the Period can be seen [$\lambda_{\max}$ is at 500 nm for In^0 (see Ref. 33) and at 440 nm for Tl^0 (see Ref. 32)]. Thus, similar regularities in the variation of the optical characteristics as a function of the positions of the elements in the Periodic System were observed both for the aquo-complexes of metals having one

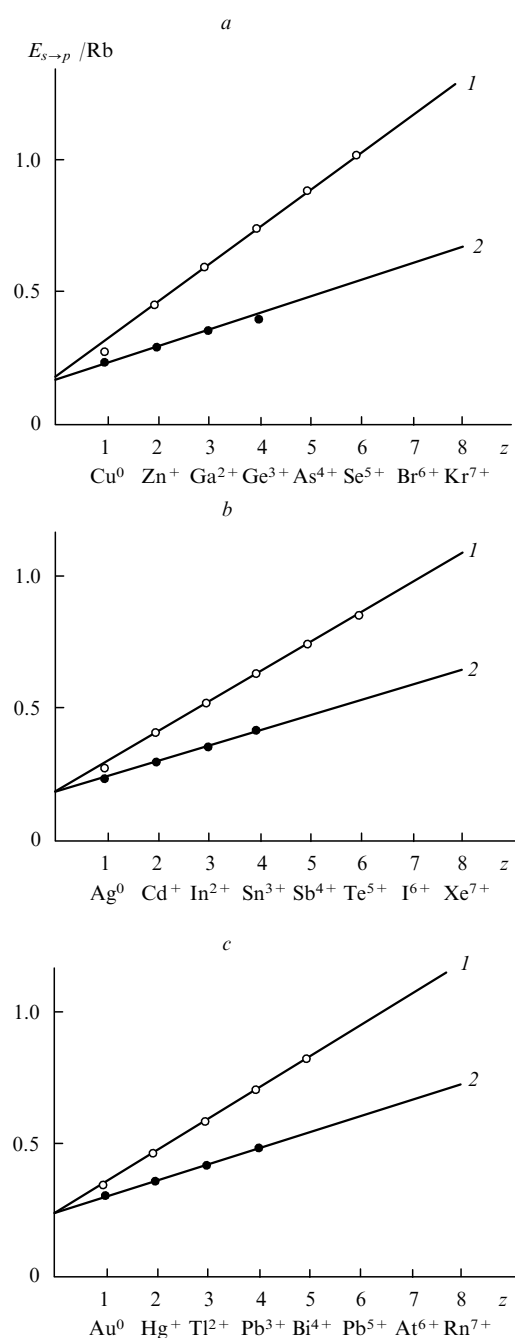


Figure 6. Dependence of the energy of the $s \rightarrow p$ transition on the charge z of the metal ions in the Fourth (a), Fifth (b), and Sixth (c) Periods. (1) In the gas phase; (2) in aqueous solution; circles — experiment; lines — calculation by Eqn (1).

electron in the outer s orbital and for the aquo-complexes with an electron in the p orbital.

2. Hydroxo-complexes

The incorporation of one OH^- ion in the coordination sphere of the metal ion leads to the splitting of the energy levels, which entails a change in the structure of the optical absorption spectrum. Apart from the main symmetrical absorption band, characteristic of the metal ion in the form of the aquo-complex, an additional broad band on the long-wavelength side is observed, as noted above. Fig. 7 presents a schematic arrangement of the energy levels for an octahedral complex, illustrating the nature of the changes in the structures of the optical transitions for mono- and di-hydroxo-complexes. The replacement of one or two water

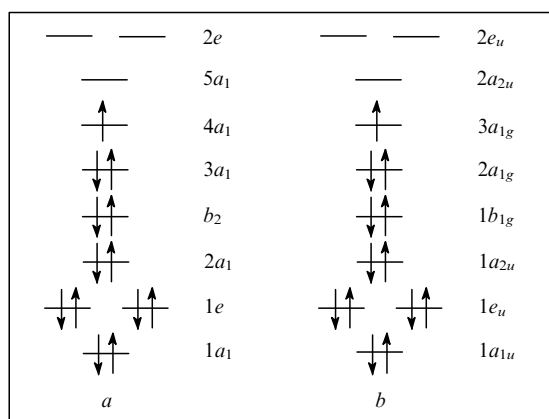


Figure 7. Schematic illustration of the energy levels for monohydroxo-complexes (a) and dihydroxo-complexes (b).

molecules by hydroxide ions respectively in position 1 (C_{4v} symmetry) or 1 and 4 (D_{4h} symmetry) leads to the splitting of the $2t_{1u}$ level. The existence of an additional transition in the hydroxo-complex is associated with a decrease in symmetry as a consequence of the appearance of new ligands. The $2t_{1u}$ level is split in such a way that the $2e$ level for $MOH^{(z-1)+}$ and the $2e_u$ level for $M(OH)_2^{(z-2)+}$ are determined by the interaction with water molecules and the energies of the $4a_1 \rightarrow 2e$ and $3a_1 \rightarrow 2e_u$ transitions respectively therefore change little compared with the energies $2a_{1g} \rightarrow 2t_{1u}$ transitions in the aquo-complexes. On the other hand, the $5a_1$ level for $MOH^{(z-1)+}$ and the $2a_{2u}$ level for $M(OH)_2^{(z-2)+}$ are associated predominantly with the interaction with OH^- ions, while the energies of the $4a_1 \rightarrow 5a_1$ and $3a_{1g} \rightarrow a_{2u}$ transition are respectively smaller than the energies of the transition observed in the aquo-complexes. It is noteworthy that in the monohydroxo-complex there is a possibility of the splitting or broadening of the band owing to the *trans*-effect. However, in the mono- and di-hydroxo-complexes, not only the nature of the disposition of the levels but also the energies of the corresponding optical transitions are fairly similar. For example, the same structures of the optical bands have been observed for the $TiOH^+$ and $Ti(OH)_2^0$ species.^{28–30}

Figure 8 presents the dependence of $E_{\lambda_{max}}$ on z for the $4a_1 \rightarrow 2e$ and $4a_1 \rightarrow 5a_1$ transitions for the monohydroxo-complexes of Sixth Period metals. The long-wavelength component of the optical absorption band has been recorded for the $TiOH^+$ and $PbOH^{2+}$ ions and it has been stated that the maxima are located at $\lambda < 220$ nm and $\lambda < 240$ nm respectively. For $HgOH$, use was made of the results of a study¹⁹ in which an additional absorption band, not found previously,¹⁸ had been observed at 360 nm. It is

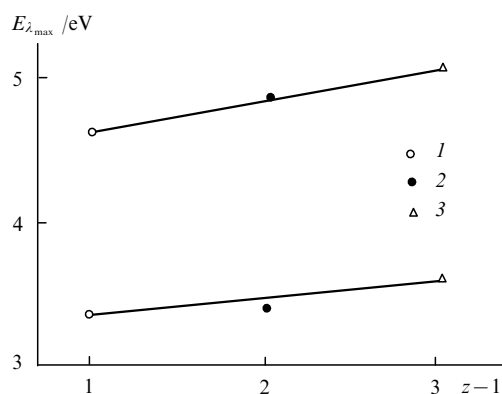


Figure 8. Dependence of $E_{\lambda_{max}}$ on the ionic charge for metal hydroxo-complexes. (1) $HgOH^0$; (2) $TiOH^+$; (3) $PbOH^{2+}$.

seen from the figure that the linearity of the dependence of the energy at the absorption maximum on z , characteristic of the aquo-complexes, holds also for the hydroxo-complexes. The difference between the transition energies in the case of the hydroxo-complexes tends to increase with increasing z , i.e. the splitting of the $4a_1$ and $2e$ levels increases with increase in the charge and with decrease in the size of the central ion.

For the fully substituted hydroxo-complexes, containing only hydroxide ions in their coordination sphere, the structure of the optical transitions is the same (with retention of the coordination numbers) as that for the aquo-complexes. The amount of experimental data for the above complexes is insufficient to establish quantitative relations. However, it is quite sufficient to demonstrate that the nature of the regularities characteristic of the aquo-complexes is retained. Thus the values $E_{\lambda_{max}} = 380,^{66} 340,^{66} 280,^{25} 275,^{26}$ and 280 and 360 nm³⁵ have been found for the $Zn(I)$, $Cd(I)$, $Ga(II)$, $In(II)$, and $Pb(III)$ hydroxo-complexes respectively. It is seen from the data presented that the optical transition energy increases with increase in z for isoelectronic ions. It also increases for equally charged ions with increase in the atomic number of the element. The decrease in the energy of the $2a_{1g} \rightarrow 2t_{1u}$ optical transition energy when water molecules are substituted by hydroxide ions is correlated with the decrease in the ionisation potentials on passing from H_2O to the OH^- ion.

3. Halide complexes

The principal characteristics of the optical transitions in the fully substituted chloride complexes of Group II–IV metals in the $^2S_{1/2}$ electronic state have been investigated by Aleksandrov *et al.*⁵⁵ HCl solutions (6–10 M), to which salts of the test metals had been added, were employed. On freezing, they gave rise to transparent glasses. After γ -irradiation at 77 K, the reduced metal ions in the $^2S_{1/2}$ electronic state appeared and their optical absorption spectra were measured in a Dewar vessel at liquid nitrogen temperature. It was established that the structure of the optical absorption is significantly more complex than the analogous structure observed for the aquo-complexes. Two–three absorption bands are observed for the metals in the Fifth and Sixth Periods. For an isotypical electronic transition, the energy at the absorption band maximum diminishes with increase in the charge on the metal ion. As stated above, similar data have been obtained by pulse radiolysis for metal halide complexes in liquid aqueous solutions. Fig. 9 presents a schematic illustration of the energy levels for a monohalide complex having C_{4v} symmetry. Compared with the schemes examined for the aquo- and hydroxo-complexes, here additional ligand molecular orbitals (MO), made up of the πp and σp atomic orbitals of the ions X^- , are present. According to this scheme, the allowed transitions in the $M(H_2O)_5X^{(z-1)+}$ complex

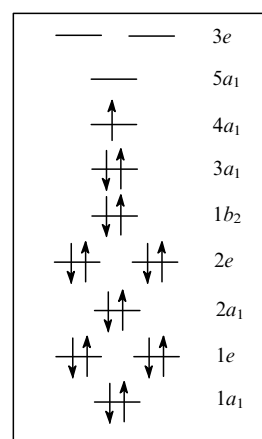


Figure 9. Schematic illustration of the energy levels for monohalide complexes.

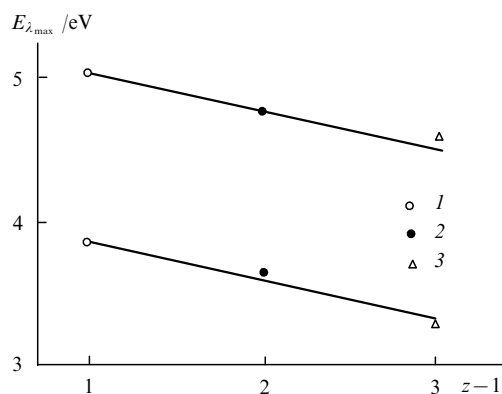


Figure 10. Dependence of $E_{\lambda_{\max}}$ on the ionic charge for metal monochloride complexes.

(1) HgCl^0 ; (2) TlCl^+ ; (3) PbCl^{2+} .

are $4a_1 \rightarrow 5a_1$ and $4a_1 \rightarrow 3e$, as well as the new transitions $2e \rightarrow 4a_1$ and $1b_2 \rightarrow 4a_1$.

Figure 10 presents the dependence of the optical transition energies for the monochloride complexes of Sixth Period metals — mercury, thallium, and lead, containing one additional electron, *i.e.* in the $^2S_{1/2}$ electronic state. Evidently, in contrast to the analogous relations for the aquo- and hydroxo-complexes, $E_{\lambda_{\max}}$ for the chloride complexes diminishes with increase in the degree of oxidation z . This factor permits the conclusion that the optical bands of $\text{MCl}^{(z-1)+}$ are determined by the $2e \rightarrow 4a_1$ and $1b_2 \rightarrow 4a_1$ transitions. The molecular orbitals $2e$ and $1b_2$ are predominantly due to ligand molecules, *i.e.* they are occupied by the electrons of the chloride ions. For metals in isoelectronic series, the energy of the abstraction of an electron increases with increase in the charge. This means that the $4a_1$ level, at which the electron is located, is lowered with increase in z . On the other hand, the $2e$ and $1b_2$ levels, at which the nonbonding electron pairs of the Cl ions are located, hardly change their positions. The energies of the above transitions in the $\text{MCl}^{(z-1)+}$ complexes in an isoelectronic series therefore decrease with increase in the degree of oxidation. The proposed model describes correctly the experimental dependence $E_{\lambda_{\max}}$ on z . In contrast to the aquo- and hydroxo-complexes in which an electron is transferred from the metal ion to the ligand molecules, in the halide complexes the electron is actually transferred from the ligand to the metal. This is the reason for the opposite type of dependence of $E_{\lambda_{\max}}$ on z for the chloride complexes of metals in the electronic state $^2S_{1/2}$ compared with the aquo-complexes.⁵⁵

For PbCl^{2+} , four optical absorption bands are observed.³⁹ This finding may be attributed to a relativistic effect. The allowed transitions at the $^2P_{1/2}$ and $^2P_{3/2}$ levels differ, as already stated, by 2.6 eV. As a consequence of this, each of the $2e \rightarrow 4a_1$ and $1b_2 \rightarrow 4a_1$ transitions undergoes additional splitting. The energies of all the transitions in the PbCl^{2+} complex are 4.56, 3.85, 3.20, and 2.54 eV.³⁹ The difference between the transition energies for paired groups of bands is indeed close to the expected value. For lighter elements, the splitting is significantly smaller and the relativistic effect is therefore manifested by a broadening of the absorption band.

For molecular monovalent mercury halide complexes (HgCl , HgBr , and HgI), two absorption bands are observed in each case, their positions undergoing a hypsochromic shift with increase in the mass (atomic number) of the halogen. Thus, whereas the absorption bands for HgCl are at 245 and 330 nm,²⁰ they are at 280 and 350 nm for HgBr ²² and at 320 and 360 nm for HgI .²³ Such variations in the energies are consistent with the proposed energy level scheme. Indeed, the electron affinity of halogen atoms diminishes in the $\text{Cl}-\text{Br}-\text{I}$ series, which corresponds to a rise in the positions of the $2e$ and $1b_2$ levels. When the position of the $4a_1$ level, which represents predominantly the atomic orbital of the

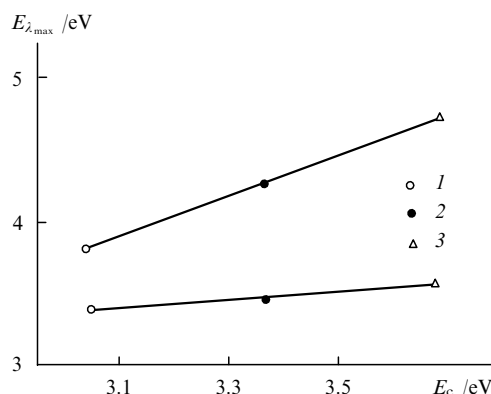


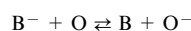
Figure 11. Dependence of $E_{\lambda_{\max}}$ for monovalent mercury halide compounds on the electron affinity (E_a) of the halogen atom.

(1) HgI ; (2) HgBr ; (3) HgCl .

metal, is retained, this should lead to a decrease in the energies of the $2e \rightarrow 4a_1$ and $1b_2 \rightarrow 4a_1$ transitions in the $\text{HgCl}-\text{HgBr}-\text{HgI}$ series, which does in fact occur. Furthermore, there is a strict linear relation between $E_{\lambda_{\max}}$ the above monovalent mercury halides and the electron affinity of the halogen atom (Fig. 11).

VI. Oxidation-reduction potentials

The direction and effectiveness of a reaction involving electron transfer is determined by the oxidation-reduction potentials of the reactants participating in it. The potential of the reaction between a reductant B^- and an oxidant O , *i.e.*



may be determined from the equilibrium constant of the reaction $K = k_+/k_-$ (here k_+ and k_- are the rate constants for the forward and reverse reactions). Metal ions in unstable oxidation states are extremely reactive and the rates of reactions with their participation are as a rule controlled by diffusion. The reactions are irreversible. The rate constants for the reverse reactions cannot usually be determined. For this reason, approximate theoretical and experimental methods are used to determine the oxidation-reduction potentials. In a theoretical calculation, it is postulated⁶⁷ that the energy of hydration of a metal ion in an unusual oxidation state depends on its radius in the same way as for alkali metal ions and the radius itself is equal to the average radius of the element preceding the given metal and that of the radius which follows it in stable oxidation states.

The experimental approach involves comparison of the characteristics of the reactions involving the reduction of particular metal ions by various radical reductants with known potentials. The potential is then estimated as the average of the potential of a reactant which led to the reduction of the metal ion and that of a reactant the presence of which did not lead to reduction. Problems concerning the determination of the oxidation-reduction potentials of metal ions in unusual oxidation states were discussed in greater detail in our earlier review.¹

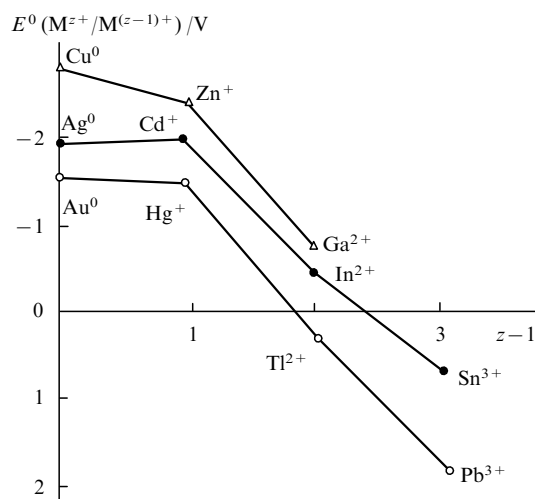
Table 4 presents the potentials known hitherto for metal ions with the $d^{10}s^1$ and $d^{10}s^2p^1$ electronic configurations. The standard potentials of metal couples in stable oxidation states [$E^0(\text{M}^{z+}/\text{M})$] as well as the analogous oxidation reduction potentials or metal couples in the atomic state [$E^0(\text{M}^{z+}/\text{M}^0)$] are also presented for comparison. In the latter case, account was taken of the correction for the energy of their sublimation at room temperature.⁶⁸ It is striking that noble metals (copper, silver, and gold) in the atomic state ($d^{10}s^1$ electronic configurations) are very powerful reductants. This is due to the presence of unpaired electrons in their outer s orbitals.

Table 4. The oxidation-reduction potentials E^0 /V.

Element	z	$E^0(M^{z+}/M)$	$E^0(M^{z+}/M^0)$	$E^0(M^{z+}/M^{(z-1)+})$
Cu	+1	+0.52	−2.6	
Zn	+2	−0.76	−1.25	−2.3
Ga	+3	−0.53	−1.36	−0.63
Ag	+1	+0.8	−1.8	
Cd	+2	−0.4	−0.81	−1.8
In	+3	−0.4	−1.05	−0.45
Sn	+2	−0.14	−1.53	
Sn	+4	+0.01	−0.67	+0.7
Au	+1	+1.65	−1.5	
Hg	+2	+0.85	+0.68	−1.5
Tl	+1	−0.34	−1.9	
Tl	+3	+0.72	+0.2	+0.3
Pb	+2	−0.126	−0.96	
Pb	+4	+0.78	+0.36	+1.8
Bi	+3	+0.22	−0.29	

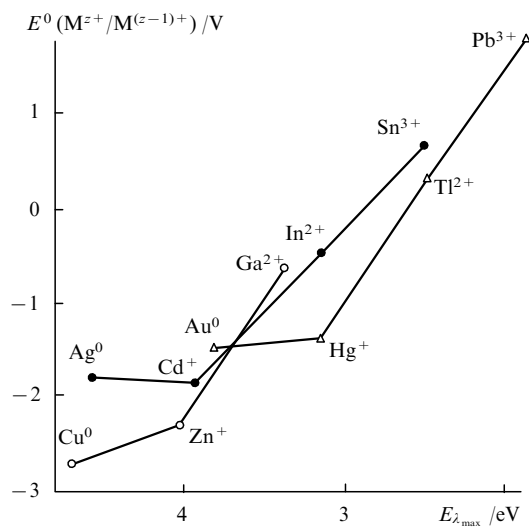
In isoelectronic series of metals, one can trace a tendency towards a decrease in potential with increase in the charge of the metal ion. Fig. 12 illustrates graphically this relation. It is seen that in each of the series of the Fourth – Sixth Periods the potential diminishes with increase in z . Whereas at the beginning of the Period copper, silver, and gold atoms are fairly powerful reductants, the metal ions at the end of the isoelectronic series, namely trivalent tin and lead, exhibit the properties of powerful oxidants. Within the limits of a subgroup, *i.e.* for equally charged ions, the potential $E^0(M^{z+}/M^{(z-1)+})$ increases steadily with increase in the number of the Period. The established type of variation of $E^0(M^{z+}/M^{(z-1)+})$ in Periods and Groups makes it possible to predict or revise the potentials for metals the oxidation-reduction characteristics of which have not been investigated. Thus, by extrapolating the linear section of the relation between the potential and the charge of the Bi^{4+} cation, it is possible to determine the potential $E^0(Bi^{4+}/Bi^{3+})$. It was found to be approximately +3.5 V, which appreciably exceeds the oxidation potential of hydroxyl radicals (2.9 V). This explains the fact, mentioned above, that OH radicals are not able to oxidise Bi^{3+} ions in highly acid aqueous solutions.

Comparison of the metal potentials $E^0(M^{z+}/M^{(z-1)+})$ with the standard potentials and the potentials for the atomic state (Table 4) showed that their variations as a function of the charge z differ significantly. For one-electron oxidation ($d^{10}s^1 \rightarrow d^{10}s^0 + e^-$), a monotonic increase in the potentials with increasing z may

**Figure 12.** Dependence of $E^0(M^{z+}/M^{(z-1)+})$ on the charge z for metal aquo-complexes.

be traced for all the Periods. This means that the stability of aquo-complexes of metals in oxidation states characterised by the electronic configuration $d^{10}s^1$ increases with increase in the number of the element in the Period. On the other hand, the variations of the standard potentials of these metals are not monotonic and reflect a complex dependence of the energies of abstraction of electrons on the degree of filling of the electron shells of the element as their number increases.

If one begins with the fact that the optical transition in an aquo-complex represents intracomplex oxidation of the metal ion, one may expect that the oxidation potential $E^0(M^{z+}/M^{(z-1)+})$ is correlated with the optical transition energy $E_{\lambda_{\max}}$. Such correspondence does indeed exist (Fig. 13). The higher the value of $E_{\lambda_{\max}}$ the more difficult it is to abstract an electron from the metal ion and the higher the oxidation potential of the latter. The correlation between $E_{\lambda_{\max}}$ and $E^0(M^{z+}/M^{(z-1)+})$ for the aquo-complexes is justified when they have the same structure and retain it as the degree of oxidation is changed. A coordination number of 2 and a linear configuration of the complexes $M(H_2O)_2$ are characteristic of the elements of the copper subgroup.⁶⁹ It may be expected that the coordination number of the elements of the next subgroup (Zn, Cd, and Hg) is six, although the aquo-complex of divalent mercury may be distorted.⁶⁹ High coordination numbers (5 or 6) may also be characteristic of the trivalent aquo-complexes in the gallium subgroup. Thus aqueous solutions of indium ions contain the complexes $In(H_2O)_5OH^{2+}$ and $In(H_2O)_4(OH)$.⁷⁰ A coordination number of 6 is also characteristic of the elements of the germanium subgroup in the +4 oxidation state. Thus the most probable coordination number of the majority of the elements considered is 6. The copper subgroup is an exception and, as can be seen from Figs. 12 and 13, this fact is apparently the reason why a deviation from the linear relation between $E^0(M^{z+}/M^{(z-1)+})$ and $E_{\lambda_{\max}}$ is observed for copper, silver, and gold atoms.

**Figure 13.** Dependence of $E^0(M^{z+}/M^{(z-1)+})$ on $E_{\lambda_{\max}}$ for metal aquo-complexes.

It is noteworthy that the correlation of $E_{s \rightarrow p}$ and $E_{\lambda_{\max}}$ (Fig. 5) makes it possible to determine from the dependence of $E_{s \rightarrow p}$ on $E^0(M^{z+}/M^{(z-1)+})$ the oxidation potentials of the aquo-complexes of metals in the electronic state $2S_{1/2}$ for which there are some kind of data concerning the positions of their absorption bands. The above approach has been used widely in the case of f elements, for which the energies of the $f^n \rightarrow f^{n-1}d^1$ transitions in the gas phase are correlated with the oxidation potentials in aqueous solution.⁷¹ The potentials E^0 of processes of the type $Zn^+ + e^- \rightarrow Zn^0$ are correlated with the energies of bands

determined by transitions from the ligand orbitals ($e_g \rightarrow t_{1u}$, etc.). They should occur in the short-wavelength region ($\lambda_{\max} < 200$ nm)

Data referring to metal ions with the $d^{10}s^2p^1$ configuration are available only for elements of the Sixth Period (Tl^0 , Pb^+ , and Bi^{2+}). By analysing the data in Table 4 for these elements, one may conclude that a similar relation, involving a decrease in the potential with increase in the charge of the cation exists for them as well.

VII. Regularities in the variation of the dissociation constants of complexes

The change in the degree of oxidation of a metal ion is accompanied by a change in its charge and size. Despite the short time during which the ion exists in an unusual oxidation state, the corresponding equilibrium coordination sphere is formed in aqueous solution. The dissociation constants of isotypical complexes of metal ions, in different oxidation states, are different. The first hydrolysis constants have been determined for many ions with the $d^{10}s^1$ and $d^{10}s^2p^1$ configurations. These constants have been compared⁷² with the corresponding constants for stable valence forms of the same metals.⁷³ It was established that the nature of the variation of the hydrolysis constants is consistent with the nature of the variation of these quantities predicted by electrostatic theory^{74,75} both for isoelectronic metal ions in the usual and unusual valence forms and for the same metals in different oxidation states. The stability of a complex is known^{74,75} to be determined by the potential energy of the interaction of two ions, which is proportional to the ratio $z_M z_L / r$, where z_M and z_L are respectively the charges on the metal ion and the ligand and r is the distance between them. Fig. 14 illustrates the variation of the first hydrolysis pK with the ratio z/r , where $z = z_M$, since the charge on the ligand (the OH^- ion) is -1 and $r = r_M + r_{OH^-}$. Evidently, the pK for isoelectronic ions in stable oxidation states, having the $d^{10}s^0$ electronic configuration, decreases linearly with increase in z/r . For elements of the Fourth and Fifth Periods, the slopes of the relations are almost the same, whilst for the elements of the Sixth Period they are significantly smaller. For metals in unstable oxidation states having the $d^{10}s^1$ electronic configuration, a similar relation is observed. However, in this case pK increase with decrease in the degree of oxidation of the metal. For example, pK increases in the sequence $Hg^+ \rightarrow Hg^{2+}$, $Tl^{2+} \rightarrow Tl^{3+}$, etc. The variation of the pK for isoelectronic series of ions in stable and unstable oxidation states is described satisfactorily by the simple equation

$$pK = \frac{q}{r} z + w, \quad (2)$$

The coefficients q and w are listed in Table 5.

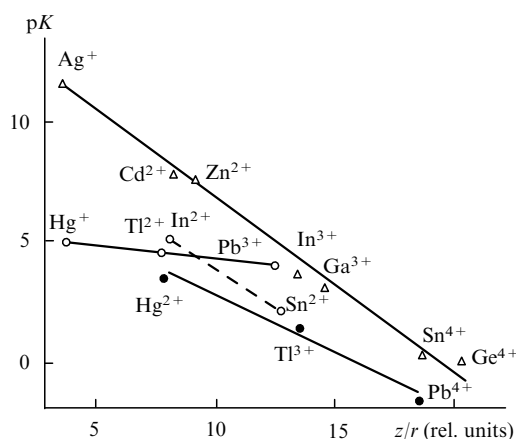


Figure 14. Dependence of the first hydrolysis constant on z/r .

Table 5. The coefficients q and w in Eqn (2).

Period	Electronic configuration	q	w
4	$d^{10}s^0$	-0.74 ± 0.2	14.2 ± 0.5
5	$d^{10}s^0$	-0.74 ± 0.2	14.2 ± 0.5
5	$d^{10}s^1$	-0.65 ± 0.1	10.0 ± 1.0
6	$d^{10}s^0$	-0.49 ± 0.02	7.7 ± 0.4
6	$d^{10}s^1$	0.13 ± 0.01	5.8 ± 0.2

The above characteristics of the variation of the pK with z/r agree with the concept of the decisive contribution of electrostatic interaction of the central ion and the ligand to the stability of the complex. For equally charged ions, the nature of the observed relations is more of an indication of the decisive role of the electronic structure. For example, a clear-cut sequence based on the increase in the pK with increasing atomic number of the element has been observed for the elements of the Sixth Period ($Hg^+ < Tl^+$, $Hg^{2+} < Tl^{2+} < Pb^{2+}$, $Tl^{3+} < Pb^{3+}$). However, for elements of the Fourth and Fifth Periods, the above relation is reversed ($Zn^{2+} > Ga^{2+}$, $Cd^{2+} > In^{2+} > Sn^{2+}$, $In^{3+} > Sn^{3+}$). Finally, one should note that the variation of the pK for equally charged ions in one subgroup is apparently not systematic (in particular, this was indicated earlier by Nazarenko *et al.*⁷³). Thus the pK of Group III elements diminish in the sequences $In^{3+} > Ga^{3+}$, Tl^{3+} and $In^{2+} > Ga^{2+} > Tl^{2+}$, while for Group II elements they decrease in the sequence $Cd^{2+} > Zn^{2+} > Hg^{2+}$.

Bearing in mind the regularities established in the variation of the pK with z/r in isoelectronic series of metals of one Period and also the nature of the variation of this quantity in equal-charge series, it appears possible to estimate the pK for certain ions. Thus $pK = 11.1 \pm 0.5$ and 6.0 ± 0.5 can be obtained for Cu^+ and Au^+ respectively by Eqn (2) from the coefficients q and w found for the corresponding Periods. The pK for the Zn^+ and Cd^+ ions are apparently very similar and are in the range 7–9.

Regularities in the variation of the instability constants, expected from electrostatic theory, have also been observed for the chloride complexes of metals in different oxidation states, including the unstable states with the $d^{10}s^1$ and $d^{10}s^2p^1$ electronic configurations.

Constant	TlCl	TlCl ⁺	TlCl ²⁺	PbCl	PbCl ⁺	PbCl ²⁺
pK_i	0.5	4.6	7.7	-0.3	1.5	2.6

Evidently the constants increase with increasing charge on the metal ion. For lead compounds, a nearly linear variation of pK_i with z/r has been noted.³⁹ For thallium complexes, pK_i is appreciably higher.⁷⁶ This means that the stability of the complexes is influenced significantly by the nature of the central ion.

VIII. Conclusion

The formation of metal ions in unusual oxidation states is not characteristic solely of aqueous media. They arise also in inorganic oxide glasses doped with thallium, cadmium, lead, or other metals as a result of oxidation-reduction reactions initiated by ionising radiation, light, or mechanical action (see, for example, the review of Aleksandrov *et al.*⁷⁷). The rigid structure of glasses is responsible for the indefinite stability of such ions. The decisive role of cooperative oxidation-reduction processes, the effectiveness and direction of which depend on the composition of the glass and its structure and the presence of free and multicentre bonds in it, has been demonstrated. It is important to note that a series of regularities which have been observed for aqueous solutions and are discussed in detail in the present review (for example, the distribution of electron densities and the optical transition energies in the isoelectronic and equal-charge series of metals) are characteristic also of inorganic oxide glasses. On the

one hand, this makes it possible to assume that the observed regularities in fundamental properties are common to all metals in unusual oxidation states and, on the other, one may assume their practical importance in the development of glass compositions with specified characteristics.

At intermediate stages of oxidation-reduction reactions in aqueous solutions, containing the ions of several metals, short-lived mixed clusters may arise. Thus, various monovalent ions, such as Cd^+ , Co^+ , Zn^+ , and Ni^+ , generated on pulse irradiation with electrons, can react with the Ag^+ ions present in the solution.^{16,78} The Zn^+ ion, which has a high reduction potential, enters under these conditions into a reaction with Ag^+ involving electron transfer and the formation of a silver atom. The Cd^+ and Co^+ ions, the potentials of which are close to that of atomic silver, form the mixed clusters $(\text{CdAg})^{2+}$ and $(\text{CoAg})^{2+}$. These clusters exist only for several microseconds and decompose rapidly with formation of Cd^{2+} (or Co^{2+}) and the Ag_2^+ cluster. In the case of Ni^+ , neither electron transfer in the reaction with the Ag^+ ion nor the formation of a simple mixed cluster have been established. However, silver is reduced with formation of a mixed product (possibly a larger mixed cluster), which appears when Ni^+ ions vanish. The appearance of mixed short-lived $(\text{AgTi})^+$ and $(\text{TiCd})^{2+}$ clusters was observed⁷⁹ in a study of the reactions of Ti_2^+ with Ag^+ and Cd^{2+} ions. The Pb^{2+} ion is reduced by Ti_2^+ with formation of the Pb^+ ion. The results obtained indicate the important, and sometimes the decisive, role of impurity ions as regards the direction or effectiveness of oxidation-reduction reactions.

Processes involving the reductive nucleation of metals (silver,^{9,80,81} copper,^{82,83} cadmium,⁸⁴ lead,³⁶ palladium,^{85,86} etc.) are associated with the initial stage involving the formation of ions in unusual oxidation states and with their dimerisation or disproportionation reaction. The chain of consecutive growth of clusters ultimately leads to the appearance of subcolloidal and then colloidal metal particles. The nucleation of silver in polymer membranes,^{87,88} in gelatin,⁸⁹ and on the surface of colloidal silicon⁹⁰ proceeds via a similar mechanism.

Certain special questions concerning the role of the anomalous valence forms of metals in catalysis have been examined in recently published reviews.^{91–93}

Thus the studies on the preparation of short-lived metal ions in unusual valence states initiated about 30 years ago have now developed further. The use of pulse radiolysis and also of the technique involving the matrix isolation of chemically reactive species made it possible not only to confirm the possibility of the appearance of these short-lived species in aqueous solutions at intermediate stages of oxidation-reduction reactions but also to investigate comprehensively their properties. In the subsequent period, main efforts were directed towards the comparative analysis of these properties and their changes within Periods and Groups of the Periodic System. This has been done most thoroughly for simple complexes of Group I–V metals in the electronic state $^2S_{1/2}$ in aqueous solutions. In particular, a regular feature of the variation of the fundamental physicochemical properties of metal atoms and ions with the $d^{10}s^1$ electronic configuration which had not been known beforehand was established and theoretically justified. It consists in the fact that the resistance of the aquo-complexes of the above metals to oxidation and also the energies of the first electronic transitions increase monotonically with increase in the ionic charge within the limits of an isoelectronic series. These and other regular features discovered apparently reflect a fundamental property of the elements, namely the monotonic variation of their physicochemical characteristics within the limits of one Period. The possibility of predicting new unusual valence forms of the elements and their properties on the basis of regular features already established is thereby justified.

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Hydrogen spillover in heterogeneous catalysis

V V Rozanov, O V Krylov

Contents

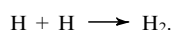
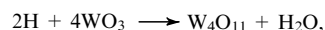
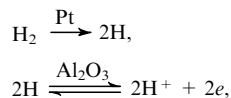
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Abstract. The phenomenon of hydrogen spillover (interphase diffusion of adsorbed hydrogen), the methods for its detection, and the factors influencing it are examined. The common occurrence of the spillover and its role in various adsorption and catalytic processes, particularly in reactions involving hydrogen on multiphase catalysts, are demonstrated. The possible mechanisms of the spillover are analysed. The bibliography includes 189 references.

I. Introduction

In heterogeneous catalysis, the term spillover is applied to the transport of active species sorbed or formed on one phase to another phase which does not sorb or generate these species under the given conditions.^{1–7} The term ‘spillover’ (from spill over in English) was introduced by Boudart *et al.*¹ The phase generating the active species is called the initiator (or activator), while the phase providing sites for the adsorption of active species is known as the acceptor. If these phases are in direct contact, then the spillover is said to be primary, but when they are separated by an additional inert carrier, it is said to be secondary.

The first direct evidence for spillover was apparently obtained by Khoobiar.² WO₃ is known to be reduced by hydrogen at temperatures above 200 °C with formation of the blue oxide W₄O₁₁. On the other hand, when pure H₂ is passed over the 0.5% Pt/Al₂O₃ + WO₃ mechanical mixture, the colour changes already at room temperature. This effect is not observed on the Al₂O₃ + WO₃ mechanical mixture. This is explained by the fact that hydrogen dissociates on platinum and migrates via Al₂O₃ onto WO₃ in the form of atoms or H⁺ ions.



Measurement of the amount of adsorbed hydrogen showed that the Pt/SiO₂ + WO₃ mixture adsorbs several times more H₂ than Pt/SiO₂ without WO₃.³ The blue colour of the tungsten oxide is due to the formation of the so called tungsten bronze under the influence of the hydrogen which has passed from Pt onto WO₃ via SiO₂ (or Al₂O₃).

The so called structural sensitivity, *i.e.* the dependence of the specific catalytic activity (calculated per unit surface or per active centre) on the particle size, is often observed in heterogeneous catalysis.⁷ This leads to differences between the specific activities of supported and massive catalysts. One of the causes of this difference may be the involvement in the reaction of the initially inactive support surface as a result of the transfer onto it of active adsorbed species via spillover.

The spillover phenomenon is common in catalysis by supported metals and mixed oxides. The atoms of not only hydrogen but also of oxygen, as well as the N, CO, NCO, and certain other species may participate in spillover. The vast majority of the communications published hitherto on this topic have been devoted to hydrogen spillover. Since 1983, international conferences on spillover are being held regularly. The present review is devoted to studies on hydrogen spillover carried out mainly during the last 10–15 years.

II. Methods for the observation of hydrogen spillover

1. Chemisorption of hydrogen

The most common method for the determination of the surface area of a metal in supported catalysts, namely from the chemisorption of hydrogen, may be used for the observation of the spillover phenomenon.³ H₂ is usually chemisorbed at 200–300 °C. Analysis of extensive experimental data showed that the number of metal atoms on the surface (*N_M*) usually corresponds to the number of hydrogen atoms adsorbed on this surface (*N_H*). The review of Sermon and Bond⁵ contains tables for different supported metals (Pt, Pd, Rh, Re, Ru, Ni), from which it is seen that the ratio *N_H*/*N_M* varies in the range 0.5–2.0. With decrease in the metal particle size, the ratio becomes less than unity in most cases, although the opposite effects are also encountered. The deviations from unity are caused by the following factors: (1) the dissolution of hydrogen in the bulk of the

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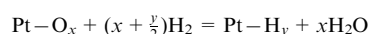
metal; (2) a change in the crystal system in small particles; (3) the presence of a relatively large number of low-coordinated atoms in small particles; (4) a change in the degree of oxidation of the metal; (5) the spillover phenomenon.

In order to elucidate the causes of the deviation of the ratio N_H/N_M from unity, hydrogen adsorption data are compared with results obtained by other methods: from the adsorption of CO, from the broadening of X-ray diffractograms, by electron microscopy, *etc.* If all the methods other than H_2 adsorption yield identical results, the possible cause of the discrepancy may be the flow of hydrogen onto the carrier. Thus the ratios $N_H/N_M = 5-10$ on the Pt/ Al_2O_3 and Pd/ Al_2O_3 catalysts⁸ and 75 on the Pt/C catalyst,⁹ found by the H_2 adsorption method, have actually been explained by hydrogen spillover.

The additional chemisorption of hydrogen on platinum deposited on an activated charcoal, occurring with increase in the duration of exposure of the catalyst to a H_2 atmosphere, is also associated with the spillover of hydrogen from platinum to the charcoal.¹⁰

Spillover may also promote an increase in the rate of adsorption of hydrogen. This phenomenon has been observed, for example, in the adsorption of H_2 on a mixture of Co/C with activated charcoal.¹¹ On the other hand, the amount of adsorbed hydrogen is determined by the capacity of the acceptor and is independent of the concentration of Co or of another initiator (Ni, Cu, Fe).

The observation of spillover by the adsorption method is favoured by a high H_2 pressure and a high temperature.⁵ Methods involving the measurement not of the amount but of the rate of adsorption of hydrogen on the support and oxygen-hydrogen titration are varieties of the adsorption method:⁵



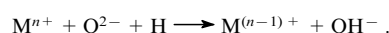
(water remains sorbed on the carrier). In the presence of hydrogen spillover, the number of adsorbed oxygen atoms N_O remains constant and N_H/N_O exceeds 2.

The surface hydrogen can also be titrated with olefins, which results in the formation of paraffins. It has been shown that at 100 °C the hydrogenation of pent-1-ene to pentane by the hydrogen adsorbed on Pt/ SiO_2 is very fast in the initial period, after which the rate of reaction falls.¹² It has been suggested that in the first stage the hydrogenation is effected by the hydrogen adsorbed on Pt, whilst in the second stage it is effected by the spillover hydrogen adsorbed on SiO_2 .

A gravimetric study of the adsorption of hydrogen and deuterium on the HNaY zeolite and on Pt/HNaY at room temperature showed that in the latter case hydrogen spillover from platinum to the zeolite takes place.¹³ The amount of hydrogen adsorbed on the platinum-containing zeolite exceeds by more than an order of magnitude the amount of H_2 capable of being adsorbed on the supported Pt. As expected, the increment in the mass of the specimen in the adsorption of deuterium was twice as great as in the adsorption of protium.

2. Reduction of oxides

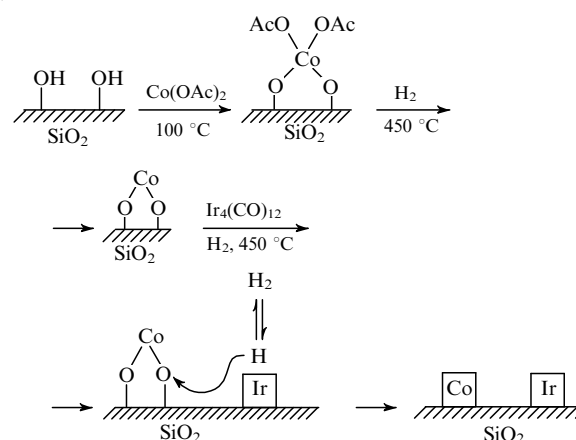
In a mechanical mixture of a supported or unsupported metal with a reducible oxide (WO_3 , MoO_3 , Fe_2O_3 , V_2O_5 , Co_3O_4 , CuO), the degree and rate of reduction may increase by virtue of hydrogen spillover:⁴⁻⁶



As a result of spillover, the reduction temperature falls in certain cases by 200–400 °C. The studies have been carried out by gravimetric, differential thermal analysis, temperature-programmed reduction, microcalorimetric, *etc.* methods. Metals (Pt, Pd, Ni, *etc.*) are thus catalysts of the reduction of oxides. The degree of reduction can be determined from the amount of reacted hydrogen and also from the changes in certain parameters characterising the solid. In the reduction of, for example, V_2O_5

to V_2O_4 , it is possible to measure the EPR signal due to V^{4+} or the area of the bands in the phase XRD spectra of the V_2O_4 phase.

In the presence of ruthenium or iridium carbonyls, the reduction of the Co/ SiO_2 catalyst, obtained from cobalt acetate, *i.e.*



is accelerated by hydrogen spillover.¹⁴ This results in the formation of a highly disperse catalyst which accelerates the hydrogenation of CO to oxygenates.

The carbide WC, the properties of which are similar to those of Group VIII metals, can also serve as the source of spillover hydrogen for the reduction of MoO_3 .¹⁵

Sulfides can also be reduced by means of the spillover. When Ni or Co is added to WS_2 , $H_{0.05}WS_2$ is formed.¹⁶

The adsorption of hydrogen on the Pt/ WO_3 catalyst has been investigated.³ It was found that WO_3 is reduced by virtue of the adsorption and activation of hydrogen on Pt and its subsequent diffusion to WO_3 . On the other hand, on pure WO_3 the adsorption of hydrogen is not observed.

On platinum deposited on the CeY zeolite, Ce^{4+} was reduced to Ce^{3+} in the presence of adsorbed perylene, perylene serving as the bridge for the transport of active hydrogen from Pt to the zeolite.¹⁷

Hydrogen spillover has also been observed in the Pt/ ZrO_2 , Pt/ SiO_2 , and Pt/ TiO_2 systems. In certain cases, spillover is promoted by the presence of water, the molecules of which may also serve as bridges for hydrogen.

When MnO_2 deposited on a SnO_2 film is heated, reduction does not occur in a H_2 atmosphere at 500 °C. According to EPR data,¹⁸ the addition of Pd leads to the appearance of Mn^{2+} as a consequence of hydrogen spillover and the reduction of MnO_2 . However, the effect of hydrogen spillover is not easy to estimate quantitatively for the examples quoted not only because of technical difficulties but also by virtue of the characteristic features of the topochemical process. Hydrogen spillover may prove to be an essential condition for reduction only in the nucleation stage, whilst in the phase growth process the reaction may be propagated by the hydrogen interacting directly with the oxide. The degree of reduction depends also on the extent of the interface between the metal catalyst and the oxide being reduced. The reduction of oxides can therefore be regarded as confirmation of the occurrence of spillover, but it does not allow quantitative estimates.

The apparent activation energy (E_a) for the reduction of oxides under spillover conditions does not differ from E_a in noncatalytic reduction. The presence of a metal apparently promotes an increase in the amount of reactive hydrogen or an increase in the rate of nucleation (in the pre-exponential factor).⁶

One of the products of the reduction of oxides is water. According to different data, it either accelerates or retards both hydrogen spillover and the reduction process itself. This also complicates the use of the oxide reduction process for the observation of spillover.

3. The influence of spillover on catalysis

Multiphase catalysts frequently possess an enhanced activity and selectivity. This can be explained by the fact that one of the stages of a complex process occurs on one phase whilst another occurs on another phase, spillover taking place between the phases (sometimes with participation of a third phase).¹⁹ In the case of hydrogenation, the supported metal may adsorb and activate hydrogen, the support may adsorb the substance to be hydrogenated, and the reaction itself proceeds on the support surface as a result of hydrogen spillover.

For example, it has been found²⁰ that the specific rate of hydrogenation of benzene per unit mass of Pd increases by a factor of 3 when the Pd/Al₂O₃ catalyst is diluted with pure Al₂O₃. Hydrogen diffuses over distances up to 0.5 mm. At -52 °C, the degree of coverage of the Al₂O₃ surface by hydrogen may reach 3×10^{-2} .

In estimating effects of this kind, one should bear in mind that they may be accounted for by the 'trapping' by the diluent of the coke which poisons the catalyst.⁵ This is also a kind of spillover but of the organic substance and not hydrogen. It has been shown²¹ that the addition of Pt to the Ni-Mo/SiO₂-Al₂O₃ system ensures an appreciable decrease in the temperature corresponding to the removal of coke after the hydrocracking of heavy oils. When Pt was added to H-Ga silicate, an increase in the rate of aromatisation of propane and a sharp decrease in coke formation were observed.²² A similar phenomenon has been noted in the alkylation of 1,2,4-trimethylbenzene and its disproportionation to durene after the addition of Pt to montmorillonite. It has been shown by IR spectroscopy that the Lewis acid centres are then converted into Brønsted acid centres.²³⁻²⁵

The increase in the rate of hydrogenation of ethene on the Pt/SiO₂ catalyst diluted with SiO₂ or Al₂O₃ has also been attributed to hydrogen spillover.²⁶ The use of Al₂O₃ as a diluent afforded a greater increment in the rate of hydrogenation than dilution with SiO₂.

As the Pt/C catalyst was diluted with pure carbon up to a ratio of 1 : 50, its activity in the hydrogenation of benzene initially rose and then became constant.²⁷

The Pt/Al₂O₃ catalyst diluted with Al₂O₃ up to ratios ranging from 1:3 to 1:100 has been tested in the hydrogenation of benzene.²⁸ It was found that the specific activity of the catalyst per gram of Pt increases with increase in dilution up to 1 : 50. The activation energy for the reaction, which is 38.5 kJ mol⁻¹, did not change on dilution. The authors²⁸ assumed that the rate-limiting stage is not spillover but the interaction of benzene with atomic hydrogen. The rate of hydrogenation of benzene on the Pt/Al₂O₃ catalyst diluted with Al₂O₃ was equal to the sum of the rates of reaction on Pt/Al₂O₃ and Al₂O₃, but the reaction does not occur on pure Al₂O₃ in the absence of platinum.

The isomerisation of n-pentane to isopentane on the Pt/SiO₂ or H-ZSM-5 catalytic systems proceeds at a low rate, but when they are mixed an active and selective catalyst of the isomerisation reaction in the presence of hydrogen is obtained.²⁹ Oligomerisation predominates in the absence of H₂. It has been suggested that hydrogen spillover is necessary for the occurrence of hydroisomerisation.

The Pt/KA + NaY mixed catalyst exhibited a much higher activity in the hydrogenation of isobutene to isobutane than Pt/KA and NaY separately.³⁰ In this case too, hydrogen spillover accelerates the catalysis.

An appreciable increase in catalytic activity in the hydrodesulfurisation of thiophene was noted when MoS₂ (or WS₂) was mixed with PtS/γ-Al₂O₃, PdS/γ-Al₂O₃, or Rh₂S₃/γ-Al₂O₃.³¹ It has been suggested that noble metals activate hydrogen, which then migrates via the spillover mechanism onto MoS₂ or WS₂, where it participates in the hydrogenation. The addition of Ru to the Co-Mo/Al₂O₃³² or MoO₃/Al₂O₃³³ catalyst has the same effect.

The rate of hydrocracking of diphenylmethane also increases after the addition of sulfided Co-Mo/SiO₂ to an silica-alumina by virtue of hydrogen spillover.³⁴

The mechanism of the cracking of n-hexane on the Pt/H-erionite bifunctional catalyst involves hydrogen spillover.^{35,36} The hydrogen dissociated on platinum migrates onto the carrier, where a dynamic equilibrium is established between the atomic and protonated forms of hydrogen.

Organic deposits on the metal surface may also serve as a suitable 'phase' for the occurrence of spillover. It has been shown by LEED (low energy electron diffraction) that the hydrogenation of C₂H₄ on Pt and Rh single crystals takes place on top of an ethylidyne layer, which remains ordered under the reaction conditions.³⁷

The hydrogen participating in spillover can also interact with organic deposits and can ensure the removal of coke.³⁸ The isomerisation of paraffins and aromatic alkyl-substituted compounds takes place on acid catalysts and the reaction stoichiometry does not require that hydrogen participates in it. However, the introduction of small amounts of Pt and H₂ into the system accelerates the process as a result of the hydrogenation of the coke which poisons the catalyst.

In a mechanical mixture of coke-saturated Al₂O₃ with Pt-Re/Al₂O₃, the hydrogenation of coke via the spillover mechanism begins at a Re concentration of 50%.³⁹

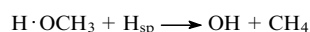
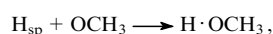
4. Isotope methods

One of the commonest methods for the observation of hydrogen spillover is isotope exchange between D₂ and the OH groups of the carrier. An increase in the rate of isotope exchange between the OH and OD groups on Pt/Al₂O₃ compared with the rate of this process on Al₂O₃ was first observed by Carter *et al.*⁴⁰ Conner *et al.*⁴¹ studied hydrogen spillover on Pt/SiO₂ with the aid of D₂ by FTIR (fourier-transform infrared) spectroscopy. Platinum was placed at the centre of pressed Pt/Al₂O₃/SiO₂ and Pt/SiO₂ discs in order to measure the concentration gradient during spillover. Experiments were carried out also in which the spillover initiator (Pt/SiO₂) was isolated from Al₂O₃.^{42,43}

The isotope exchange between deuterium and the OH groups of a Y zeolite has been investigated by FTIR spectroscopy.⁴⁴ A two-component Pt/NaY-HNaY specimen was used for this purpose. The H-D isotope exchange on the surface of the HNaY zeolite was observed only when the latter was in direct contact with the platinum-containing component of the Pt/NaY specimen. At room temperature, the process was limited by the diffusion of deuterium and by the H-D exchange proper.

Tritium has also been used in the study of spillover.⁴⁵ Investigation of the interaction of ¹⁴C₂H₄ and ¹⁴C₃H₆ with T₂ on Pt/SiO₂ and Pt/Al₂O₃ showed that the OH groups of the support exchange with tritium under the hydrogenation conditions and that the degree of involvement of Al₂O₃ in this process is greater than that of SiO₂.

Transmission IR spectroscopy has been employed to investigate the exchange of the OH and OD groups of the Rh/Al₂O₃ catalyst in a stream of D₂.⁴⁶ The exchange of methoxylated OH groups with hydrogen on SiO₂ was observed when SiO₂ was mixed with Pt/SiO₂.^{47,48} The formation of methane as a result of the interaction of the methoxy-groups with hydrogen (demethoxylation) via a mechanism involving spillover has been noted:



(H_{sp} = spillover hydrogen).

5. The scavenger method

By adding to the system substances which interact quantitatively with hydrogen and by using sensitive methods such as, for example, EPR as indicators, it is possible to reduce greatly the threshold in the observation of the spillover effect. This has been confirmed by the results of a study on the CeY zeolite + Pt black system,⁴⁹ where Ce⁴⁺ was reduced to Ce³⁺ in the presence of hydrogen. The adsorption of perylene or anthracene led to the

appearance of radicals, readily detectable by EPR. When spillover occurs, the radicals are hydrogenated and the EPR signal vanishes.

Weakly bound H atoms, participating in the hydrogenation of benzene, have been detected by depositing *N-tert*-butyl- α -phenylnitron or 2,4,6-tri-*tert*-butylnitrobenzene, which served as 'traps' for H atoms, on Pd/Al₂O₃.⁵⁰

6. Thermodesorption methods

The temperature-programmed desorption (TPD) and temperature-programmed reaction (TPR) methods can also be used to observe the spillover of adsorbed species.⁵¹ The nonstationary temperature regime employed in these methods makes it possible to separate in time processes occurring on the surface at different rates, including processes involving the desorption of the initial substances, adsorbed in one form or another, and their conversion into other products via different pathways. In contrast to unsupported catalysts, on supported catalysts there is a possibility of the spillover of adsorbed species. This is manifested either by a simple increase in the areas of the TPD peaks due to the substances adsorbed beforehand or by the appearance of new additional peaks.

The TPD – TPR methods yield direct information about the amount of the substance which has diffused onto other phases and make it possible to calculate the coefficients of surface diffusion and the activation energy for the process.

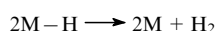
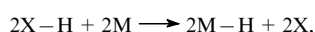
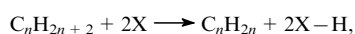
The use of stable isotopes significantly expands the possibilities of the TPD and TPR methods in the study of the mechanism of the spillover of adsorbed species. These methods have been used to investigate hydrogen spillover on a wide range of supported catalysts: platinum,^{52–57} palladium,⁵⁸ nickel,^{52–57} and rhodium⁵² on aluminium, titanium, and silicon oxides, cobalt and molybdenum on aluminium oxide⁵⁹ and activated charcoal,⁶⁰ and platinum on zirconium oxide.⁶¹

7. Reverse hydrogen spillover

This term is frequently used to designate the reverse migration of hydrogen from the support to the metal.

In the adsorption of an olefin on 0.03% Pt/H_xWO₃ at 100 °C, hydrogen is removed from the catalyst, its amount corresponding to the ratio $N_{\text{H}}/N_{\text{Pt}} = 277$.⁵ Since H_xWO₃ is incapable of hydrogenating the olefin at this temperature, the participation of hydrogen in the hydrogenation can be accounted for by its reverse spillover from H_xWO₃ onto Pt. In H_xWO₃ + Pt/SiO₂ mixtures, where there is little contact between Pt and H_xWO₃, the reverse spillover was not observed.

The desorption of hydrogen from carbon^{11,62,63} or from the H – ZSM-5 zeolite⁶⁴ is accelerated when platinum or a metal sulfide are deposited on them. The dehydrogenation of cyclohexane under these conditions (at 450 °C) is associated with the reverse spillover of hydrogen from the support to the metal. The catalytic activity increases with increase in the initiator concentration and reaches a certain limit, which is independent of either the amount or nature of the initiator. The reverse spillover may be the rate-limiting stage in the dehydrogenation reaction proceeding via the mechanism



(X is the carbon surface and M is the metal).

Ga³⁺ and Zn²⁺ ions may play the same role of accelerators in the recombination of H atoms, because the rate of aromatisation increases on mixing Ga₂O₃ or ZnO/Al₂O₃ with ZSM-5.^{65–70} This entails the reverse hydrogen spillover from the aromatic compound, adsorbed on the zeolite, to Zn²⁺ and Ga³⁺, which accelerate the recombination of H atoms.

III. The influence of various factors on hydrogen spillover

1. The influence of water, oxygen, CO, and other compounds

Many investigators noted a significant influence of water on hydrogen spillover.^{1,3,5,71} Tungsten trioxide is reduced by hydrogen to the blue oxide at temperatures above 400 °C. If WO₃ is mixed with platinum black, the reduction temperature falls to 100 °C and, when water is adsorbed in addition, reduction begins already at room temperature. This effect can be naturally attributed to the positive influence of H₂O if, as stated above, hydrogen spillover occurs with participation of the OH groups of the support. In practice, both positive⁷¹ and negative⁷² effects of water have been observed. According to Cevallos-Candau and Conner,⁷³ water accelerates the exchange between the OH and OD groups on the support but not spillover as such.

Oxygen and CO inhibit spillover.^{74,75} Oxygen interacts with hydrogen to form water, which lowers the rate of spillover.⁶ However, the reduction of WO₃ was not observed in the WO₃ + Pt black mixture at room temperature in the presence of H₂.⁷⁶ On the other hand, the addition of oxygen to hydrogen or the adsorption of oxygen before the admission of H₂ alter the colour of WO₃, to blue, which may indicate the reduction of the oxide.

It has been shown⁷⁷ that mobile oxygen, adsorbed on the Pt/TiO₂ catalyst under the conditions of the oxidation of the latter, increases hydrogen spillover in this system.

The accelerating effect of water on the OH – OD exchange in the Pt/Al₂O₃ system in the presence of D₂ at 150 °C has been observed with the aid of chromatographic methods.⁷⁸ In the absence of platinum, no exchange was observed.

An increase in the rate of hydrogen spillover on the Pt/MoO₃ catalyst, obtained by impregnating MoO₃ with a solution of chloroplatinic acid,^{79–81} promoted a decrease in the concentration of residual chlorine on heat treatment.

2. Spillover initiators

Hydrogenation catalysts are as a rule hydrogen spillover initiators: Pt, Pd, Ni, Rh, CuCr₂O₄, etc. The presence of even very small amounts (of the order of 10^{–4}%) of a metal (Ni, Pd, Pt, W) in SiO₂ may induce an appreciable absorption of H₂ at 1000 °C (the number of atoms of the absorbed hydrogen exceeds by a factor of 100 the number of metal atoms).⁸²

The bond between hydrogen and the initiator metal should not be unduly strong and the catalyst must be sufficiently dispersed to ensure good contact between the metal and the accepting or transport phases. The activity of metals in the exchange between D₂ and the OH groups of pentasil varies in the sequence Pt > Pd > Ni, which is consistent with the greater strength of the Ni – H bond compared with the Pt – H and Pd – H bonds.⁸³

In the mixed Co – Mo – S and Ni – W – S catalysts, the hydrodesulfurising initiators of hydrogen spillover are apparently Co and Ni sulfide phases. Rh₂S₃, PdS, and PtS_x mixed with MoS₂ or WS₂ can also serve as spillover initiators.⁸⁴

The spillover initiators (donors of spillover species) do not necessarily have to be mixed with the acceptor; they can also be separated in space from the latter after the initial activation.

Special experiments have been carried out with separation in space of the source and acceptor of the spillover species.^{6,85,86} The Pt/Al₂O₃ catalyst was placed in a bulb separated from the SiO₂ acceptor by a porous partition. After activation by heating in a hydrogen atmosphere at 430 °C, the bulb with the catalyst was removed from the activation zone and ethene, ethyne, heptane, benzene, or cyclohexadiene were hydrogenated on SiO₂ at a lower temperature (200 – 270 °C) with participation of spillover hydrogen. The amount of the latter was 10¹² H atoms per gram of SiO₂. Such an activated SiO₂ specimen retained its activity in the C_nH_m + H₂ reaction for a long time, whereas on nonactivated SiO₂ the above mixture did not react. Hence it follows that

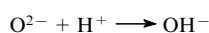
hydrogenation proceeds mainly with participation of hydrogen from the gas phase on centres created by virtue of spillover. Careful analysis demonstrated the absence of the Pt impurity in SiO₂ after spillover.

Cumene was cracked similarly on SiO₂ after its initial activation by the spillover hydrogen generated by the Pt/Al₂O₃ system.⁸⁷

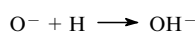
Similar results were obtained with the aid of Al₂O₃ activated by the spillover hydrogen flowing from the Pt/Al₂O₃ catalyst.^{6,88} A similar activation but at a lower temperature may be ensured by Ni/Al₂O₃.

3. Hydrogen acceptors

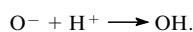
In many cases, the final result of hydrogen spillover is the formation of new hydroxy-groups. Consequently oxygen ions may serve as acceptors of hydrogen atoms or ions:



or



or



On oxides coated with a hydroxyl layer, structural defects serve as acceptor centres. Carbon is also a good acceptor.

It was already stated above that adsorbed unsaturated compounds and the metal oxides themselves may function as acceptors of H atoms. If protons participate in the spillover, then the effectiveness of the acceptors is determined by their proton affinity,⁸⁹ which varies in the sequence water = methyl alcohol > n-butyl alcohol > *tert*-butyl alcohol ≫ dibutylamine.

4. Promoting agents

Transport bridges or phases may serve as mediators for the transfer of H atoms from the donor to the acceptor. In one of the first studies on spillover,⁹ it was found that the transport of hydrogen on the Pt/C catalyst is accelerated by carbon contaminations, which are produced after the isomerisation or hydrogenolysis of neopentane. The carbon contaminations act as bridge between Pt and C. Their combustion inhibits the spillover. Above it was already stated that perylene also serves as a bridge for the transport of H atoms between Pt and the CeY zeolite.^{10,17} Such bridges may be water and the OH groups of the support. There are data showing that SiO₂ plays more effectively the role of a bridge for the transport of H atoms than Al₂O₃. In the hydrogenation of ethene on the Pt/SiO₂ + H_xWO₃ system, the WO₃ phase transfers hydrogen to C₂H₄. Carbon functions as a bridge in the Pt/C catalyst.

IV. Kinetics of hydrogen spillover

1. The number of hydrogen spillover adsorption centres

Measurement of the excess amount of adsorbed hydrogen compared with the amount necessary for monolayer coverage of the metal surface makes it possible to determine the number of support centres participating in spillover. The study of the adsorption of H₂ on Pt/Al₂O₃ at 250–300 °C by a volumetric method showed⁹⁰ that the number of spillover centres N_{H} is 10¹² cm⁻². Data for the TPD of hydrogen on a similar catalyst yielded $N_{\text{H}} \approx 2 \times 10^{12}$ cm⁻².⁵⁷ A similar value (1.5×10^{12} cm) was obtained by NMR in experiments on the adsorption of H₂ on Pt/SiO₂ at room temperature.⁹¹ Thus the number of centres N_{H} on oxides corresponds to ~1% of the total number of surface centres, which is much less than the number of OH groups on the surface.⁶

On Pt/C, N_{H} is much greater — from 10¹³ to 10¹⁶ cm⁻² (or from 0.01 to 10 formal monolayers).^{9–11}

In experiments where the Pt/SiO₂ source of spillover was isolated from Al₂O₃, it was shown that, under the conditions of the OH–D₂ exchange, hydrogen is transferred over a distance of

1 cm in several minutes.⁴² In the hydrogenation of C₂H₄ on the Pt/SiO₂ + SiO₂ system, the induction of activity on the SiO₂ surface requires prolonged exposure in H₂ (more than 17 h at 400–460 °C) and is characterised by an activation energy of 117 kJ mol⁻¹.⁴³

2. Kinetics of catalytic reactions occurring under the conditions of hydrogen spillover

The kinetics of the chemisorption of hydrogen on Pt/Al₂O₃ have been investigated.^{57,91} It was found that the amount of absorbed hydrogen is proportional to the square root of the adsorption time and that surface diffusion is apparently the rate-limiting stage.

When the hydrogenation reaction proceeds under stationary conditions, the overall activity of the supported metal greatly exceeds (by 1–2 orders of magnitude) the activity of the acceptor-diluent. Spillover should not therefore influence significantly the rate of hydrogenation. The situation is different when hydrogen and the substance hydrogenated are adsorbed on different phases. Spillover exerts a major influence on the kinetics also when the surface is reduced and the active centres are formed with participation of hydrogen arriving from another phase. Delmon⁷⁹ called this phenomenon ‘remote control’.

It was found⁹² that two kinds of spillover hydrogen exist on Pt/Al₂O₃ at 450 °C — irreversible and reversible. The rate of aromatisation of n-hexane is proportional to the surface concentration of irreversible spillover hydrogen, while the rate of hydrocracking and isomerisation is proportional to that of reversible spillover hydrogen.

A mathematical model of spillover has been examined by Edvinsson *et al.*⁹³ It was postulated that the reaction proceeds on the metal serving as the source of spillover species and that the carrier stores these species and interacts with the metal via the spillover and reverse spillover mechanisms. The application of the cyclic modulation method made it possible to discriminate between processes occurring with and without the participation of spillover.

According to a similar model proposed by Nam and Silverston,⁹⁴ there are two regions in the catalysts: active (metal) and inactive (carrier). Dissociative adsorption, the reaction, and recombination desorption take place in the active region. The dissociated species migrate to the inactive part, which serves as a reservoir for the latter, and conversely. The model predicts that, in the absence of spillover, the yield should monotonically decrease with increase in modulation frequency, whilst in the presence of spillover it should pass through a maximum.

Mathematical analysis of the overall kinetic model of a two-stage reaction at a surface incorporating sites of two types with different heats of adsorption showed that the spillover of the adsorbed species between these sites may lead to both an increase and a decrease in the rate of the chemical reaction.⁹⁵ In the oxidation of carbon monoxide on such a heterophase surface, the kinetic coupling of the reaction, induced by CO spillover, leads to an appreciable alteration of the temperature dependence of the reaction rate and also to the appearance of superadditive activity at low temperatures.⁹⁶

3. Determination of diffusion coefficients

The TPD,⁵⁷ adsorption,⁹⁷ electron microscope,⁹⁸ and NMR^{91,99} methods have been used to determine the diffusion coefficients of hydrogen. A table of the diffusion coefficients D_{H} for a series of oxides has been published in a review⁵. At room temperature, $D_{\text{H}} = 10^{-10}$ cm² s⁻¹ on CeY.¹⁷ At 50 °C, $D_{\text{H}} = 10^{-16}$ cm² s⁻¹ on WO₃ and 10^{-13} cm² s⁻¹ on MoO₃.⁹⁷ At 100 °C, $D_{\text{H}} = 10^{-14}$ cm² s⁻¹ on carbon and SiO₂, while the activation energy is $E_{\text{D}} = 65$ kJ mol⁻¹.⁹⁸ At 400 °C, $D_{\text{H}} = 10^{-15}$ cm² s⁻¹ and $E_{\text{D}} = 119$ kJ mol⁻¹ on Al₂O₃ and diffusion takes place over a distance up to 200 nm from the Pt particles.⁹⁸

According to NMR data, 10¹² hydrogen atoms participate in the spillover on Pt/SiO₂ over each square centimetre of the SiO₂ surface⁹¹ and, since the average distance between the Pt particles

on the catalyst is 180 nm, the spillover extends over a distance of at least 90 nm.

Data on the kinetics of the exchange between the OH groups of the support and D_2 are usually employed for the determination of D_H . For this purpose, it is necessary that the direct exchange without the participation of the metal should be negligible, that the migration on the support should be the rate-limiting stage, and that the surface diffusion should differ from the bulk-phase diffusion.¹⁰⁰

If the surface concentration of H atoms on the initiator metals c_H is constant, then D_H can be calculated by the equation⁵⁷

$$Q = c_H I_0 \sqrt{\pi D_H t},$$

where Q (atoms g^{-1}) is the number of species which have diffused onto the support during the time t and I_0 ($cm\ g^{-1}$) is the perimeter of the metal particles. At 400 °C, $D_H = 9.3 \times 10^{-11}\ cm^2\ s^{-1}$ on Rh/SiO₂, $1.7 \times 10^{-10}\ cm^2\ s^{-1}$ on Rh/Al₂O₃, $2.2 \times 10^{-10}\ cm^2\ s^{-1}$ on Rh/ZrO₂ and $8.0 \times 10^{-10}\ cm^2\ s^{-1}$ on Rh/CeO₂.¹⁰⁰

Significantly higher hydrogen diffusion coefficients are also encountered. For example, it has been found⁷³ that $D_H = 10^{-3}\ cm^2\ s^{-1}$ on Pt/SiO₂ at 200 °C. Such appreciable differences between the diffusion coefficients are most probably associated with differences not taken into account under the experimental conditions.

V. The mechanism of hydrogen spillover

1. The surface and gas-phase pathways to spillover

The question of the possible transfer of hydrogen atoms during spillover not along the surface but through the gas phase arose already in the first studies. According to the data of Dmitriev *et al.*,¹⁰¹ in the isotope exchange between deuterium and surface OH groups of the HNaY zeolite the activated deuterium is transported not through the gas phase but along the surface of the support separating the spillover initiator (Pt) and the zeolite.

Gadgil and Gonzales¹⁰² investigated the adsorption of the hydrogen atoms obtained in the high-temperature heating of tungsten in a H₂ atmosphere. It was found that the rate of adsorption is low and independent of the type of carrier, which most probably constitutes evidence against the transfer of H atoms through the gas phase. The study of the adsorption of hydrogen atoms generated in a microwave discharge¹⁰³ on Pt/TiO₂ showed that F centres, capable of effecting the hydrogenation of ethene, are formed in TiO₂ under the influence of these atoms. The low rate of adsorption of H atoms on the Pt/zeolite system is due to the fact that only the outer surface of the catalyst interacts with these atoms.¹⁰⁴

The conversion of CO into methane in a two-bed reactor, the lower section of which contained the Pt/zeolite X catalyst in a stream of H₂ in a stationary bed while the upper section contained the Ni/zeolite X in a stream of CO + H₂, occurred at a much higher rate than in the absence of platinum.¹⁰⁵ The authors did not reach a definite conclusion about the transfer of hydrogen atoms through the gas phase, noting the possibility of their diffusion through the glass lattice separating the two beds.

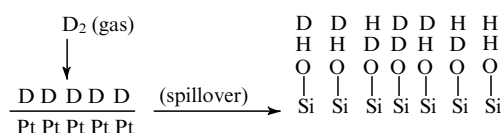
If SiO₂ is treated with hydrogen at a temperature above 800 °C in the presence of various metals but without being in contact with them, then the siloxane bridges Si—O—Si are converted into S—H groups.¹⁰⁶ This phenomenon has been explained by the transport of the metal on SiO₂ with participation of water vapour. In terms of their activities, the metals can be arranged in the sequence Ta > Ni > Pt > W.

Hypotheses concerning the gas-phase transport of H atoms at relatively low temperatures have been put forward in only a few investigations. In the study of Baumgartner *et al.*,¹⁰⁷ these hypotheses were based on experiments involving the reduction of anthracene and anthraquinone adsorbed on SiO₂ separated in space from the source of hydrogen — Pd/SiO₂. Rodriguez and Baker¹⁰⁸ concluded that at room temperature and a pressure of 0.2 mm Hg atomic hydrogen is transferred from metal sulfides

(MoS₂, FeS₂, or FeS) through the gas phase onto a graphite surface separated from them. However, since the desorption of hydrogen atoms at low temperatures is thermodynamically unfavourable, one cannot rule out that hydrogen is transferred from the source to the acceptor not directly but in the form of other species (OH, H₂O, *etc.*) in these cases too.

2. The mechanism of the diffusion of hydrogen on an oxide surface

One of the first studies on the spillover mechanism was undertaken by Conner *et al.*,⁴¹ who used for this purpose FTIR spectroscopy *in situ*. The diffusion of the deuterium adsorbed on Pt/SiO₂ from Pt to the carrier was followed from the exchange between D atoms and the OH groups of SiO₂. It was postulated that the process proceeds in accordance with the scheme



The heat of adsorption of H₂ on Pt was 115 kJ mol⁻¹ and the activation energy was 67 kJ mol⁻¹. The heat of adsorption of H₂ on SiO₂ was smaller — 12.5 kJ mol⁻¹. Thus the transfer of deuterium from platinum to the support is an endothermic process and spillover occurs by virtue of the existence of a high deuterium concentration gradient at the interface between Pt and the support. However, it is possible that the heats of adsorption of H₂ on the real spillover centres greatly exceed 12.5 kJ mol⁻¹. Under the experimental conditions, the ratio of different forms of deuterium was

$$PtD : D_{sp} : OD = 1 : 5 : 600 \quad (D_{sp} = \text{spillover deuterium}).$$

It has been postulated that the spillover on SiO₂ takes place via the formation of associative complexes with participation of pairs of OH groups (vicinal or geminal).⁴³

Analysis of diffuse scattering IR spectra showed¹⁰⁹ that the adsorption of H₂ (D₂) on 10% Pt/TiO₂ at a low temperature results in the appearance of a new broad absorption band at ~ 3000 (2300) cm⁻¹. The authors assigned it to the OH (OD) groups at the metal–support interface. This band is thermally unstable and at room temperature the OH and OD groups are readily involved in exchange with D₂ and H₂ respectively.

The involvement of the OH groups of the HNaY zeolite in the spillover of deuterium in the HNaY + PtNaY system has been demonstrated by FTIR spectroscopy *in situ*.^{110, 111}

Under the conditions of the hydrogenation of ethene on Pt/Al₂O₃, the ethene reversibly adsorbed on the support reacts with the hydrogen arriving from platinum via the spillover mechanism.¹¹² Methylation of the support hydroxyls with diazomethane greatly reduces the rate of the reaction. The Pt/Al₂O₃—OCH₃ system formed after modification is at least ten times less active than Pt/Al₂O₃ and the hydrogenation reaction is propagated only by the metal on which ethene is strongly adsorbed. This demonstrates the need, in principle, for the spillover of hydrogen in order that the given reaction may be catalysed.

The majority of investigators hold to the view nowadays that hydrogen atoms participate in spillover.^{17, 101, 113} It has been found¹⁷ that the rate of disappearance of the EPR signal of perylene corresponds to the rate of adsorption of H₂ by the Pt/CeY system. We may note that the direct detection by EPR of H atoms on the majority of supports is possible only at temperatures below -170 °C. Careful analysis of the form and magnitude of the shift in the ¹H NMR spectra made it possible to establish¹¹³ that hydrogen migrates on the SiO₂ surface in the form of the H[•] radical species. The hydrogen radical species adsorption centres may be either F centres or the (SiO)- or Si-groups.

It has also been postulated that spillover proceeds via a proton mechanism.^{71, 89, 114} This is indicated by the correlation between the rate of spillover and the proton affinity of the promoting agent,^{71, 89} which may solvate the diffusing proton: $\text{H}_2\text{O} \gg \text{CH}_3\text{OH} > \text{C}_2\text{H}_5\text{OH} > \text{n-C}_3\text{H}_7\text{OH} > \text{n-C}_4\text{H}_9\text{OH}$. In the presence of all these promoting agents, the rate of spillover was independent of the specific surface of the supported Pt, while in the presence of CH_3COOH , which has a low proton affinity, such dependence was observed. In the latter case, the rate of reaction may be determined by the rate of solvation of the proton.

Bianchi *et al.*,⁴⁷ who investigated the hydrogen transfer from the Pt/ Al_2O_3 catalyst to a methoxylated silica gel (Aerogel), even postulated the involvement of H_3^+ species in spillover on the basis of kinetic data.

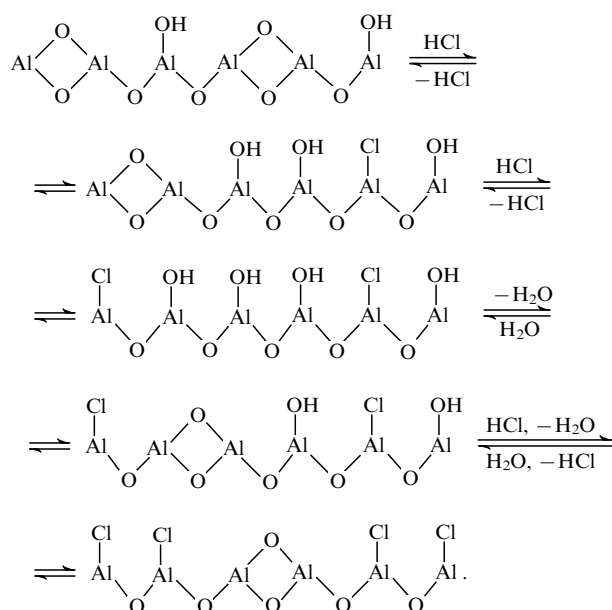
The adsorption of hydrogen on Rh/ TiO_2 has been investigated by NMR.^{74, 115, 116} Hydrogen was adsorbed in two forms: the reversible form bound to the support and the irreversible form bound to the metal. According to NMR data, hydrogen bound covalently to Pt is present at the Pt/ SiO_2 surface.⁹¹ Paramagnetic hydrogen, which reduces the relaxation time of the Si—OH bonds, participates in spillover. On Pt/ SiO_2 , two hydrogen NMR signals were also found: one corresponded to the Pt—H bond and the other to the spillover hydrogen located at the same sites as the hydrogen of the OH groups.¹¹⁷

The study of the exchange between D_2 and the OH groups of conducting supports on which platinum had been deposited failed to reveal appreciable differences between *n*- and *p*-semiconductors,¹¹⁸ which permitted the conclusion that uncharged species are involved in spillover.

The rate of the $\text{H}_2 + \text{D}_2$ exchange on Pt or Pd, deposited on a zeolite with a modulus of 30, exceeded by several orders of magnitude the rate of exchange between D_2 and OH groups.⁸³ Thus the activation of D_2 does not limit the gas-phase exchange. Spillover of hydrogen should include the interphase transfer of the activated D_2 , the migration of D on the surface, and recombination.

According to the data of Parera *et al.*,³⁸ the H—D exchange on Rh/ Al_2O_3 proceeds in two stages: rapid spillover from Rh to Al_2O_3 takes place in the first stage, while the second involves a slow exchange between the spillover hydrogen and the OH groups of Al_2O_3 .

Information about the number of spillover centres may be obtained from data¹¹⁹ on the adsorption of H_2 on Pt/ Al_2O_3 —Cl, Al_2O_3 , and their mixtures at 500 °C. The presence of chlorine alters the rate of spillover. For a certain chlorine content, maximum spillover is observed:



The rate-limiting stage is the surface migration of H atoms. The above scheme shows that, in the presence of a low chlorine content, the number of spillover centres increases, diminishing in the presence of a high chlorine content. When all the OH groups have been replaced by Cl, the protons lose their mobility owing to the absence of surface OH groups.

According to NMR data, the hydrogen adsorbed on the $\text{CuO} + \text{Cr}_2\text{O}_3$ system is capable of hydrogenating isoprene to isobutene. This hydrogen does not enter into the composition of the OH groups and does not exist on pure Cr_2O_3 . It apparently arises from the metallic copper formed under the reaction conditions.¹²⁰

It is generally believed that the first stage of the process is the homolytic rupture of the H—H bond on the metal regardless of the involvement of hydrogen atoms or H^+ ions in the spillover.

Different investigators postulate that one of two stages may limit the spillover: either the surface diffusion on the acceptor or the transfer of species from the initiator to the acceptor. Since the activation energies for these elementary stages may be different, the variation of temperature may entail also a change in the rate-limiting stage of the spillover.⁸⁵ The cause of the change in the rate-limiting stage may be also the presence at the surface of spillover promoting or inhibiting agents. A more common view is that spillover is limited by the diffusion at the support surface.⁶

3. The mechanism of the diffusion of hydrogen into the bulk phase of oxides

When small amounts of Pt or Pd are added to the oxides WO_3 , MoO_3 , or V_2O_5 , in the presence of hydrogen, tungsten (H_xWO_3),^{5, 6, 121} molybdenum (H_yMoO_3),^{6, 122–127} and vanadium ($\text{H}_z\text{V}_2\text{O}_5$)¹²⁸ bronzes are formed. They exhibit a catalytic activity in the hydrogenation of ethene, the rate-limiting stage of which may be the reverse spillover of hydrogen on Pt, where the hydrogenation reaction actually occurs.⁶

According to X-ray diffraction data, the initial monoclinic structure of WO_3 is converted into the cubic structure of $\text{H}_{0.4}\text{WO}_3$ as a result of hydrogen spillover. Hydrogen atoms occupy the hexagonal vacancies in WO_3 . The diffusion coefficient of hydrogen in the tungsten bronze is $1 \times 10^{-7} - 7.9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ at room temperature.^{99, 122}

The study of the interaction of H_2 with the (100) face of MoO_3 at a very low pressure ($10^{-5} - 10^{-8} \text{ mm Hg}$) showed¹²³ that the monoclinic bronze $\text{H}_{1.6}\text{MoO}_3$ is formed in three stages: (1) initiation, (2) a stage characterised by a constant rate of absorption of H_2 , and (3) the concluding stage of the formation of the new phase in which the rate of absorption of hydrogen diminishes. The spillover of H_2 from Pt is observed only in the first stage. Under these conditions, hydrogen permeates into the near-surface layers of the oxide. It then reacts with the oxide without the participation of Pt. The diffusion coefficient of H atoms in the second stage is 7–10 orders of magnitude higher than the coefficient usually observed in spillover.

The rate of hydrogenation of ethene on Pt/ H_yMoO_3 increases with increase in the Pt concentration.¹²⁴ According to other data, the $\text{H}_{1.6}\text{MoO}_3$ bronze may catalyse the hydrogenation of C_2H_4 also in the absence of Pt.¹²⁵ The initial rate of reaction at 160 °C on $\text{H}_{1.6}\text{MoO}_3$ is approximately the same as on Pt/ H_yMoO_3 . In the course of the hydrogenation of C_2H_4 by the hydrogen entering into the composition of the $\text{H}_{1.6}\text{MoO}_3$ bronze, the latter is converted into $\text{H}_{0.9}\text{MoO}_3$, which has a different structure. In the presence of hydrogen in the gas phase, the bronze did not undergo structural changes. The activation energy for hydrogenation was 54 kJ mol^{-1} and was close to the activation energy for the diffusion of H atoms in the bronze.¹²⁵

On Pt/ $\text{H}_y\text{VMoO}_{5.5}$ with $2.85 < y < 3.31$, the spillover hydrogen forms with the surface a very weak, apparently physical, bond with $\Delta H < 12.5 \text{ kJ mol}^{-1}$ or is occluded between the oxide layers.¹²⁸ When $y = 5.85$, the heat of adsorption of hydrogen is $127.6 \text{ kJ mol}^{-1}$.

The vanadium bronze $\text{H}_{3-3.8}\text{V}_2\text{O}_5$ is X-ray-amorphous and, in contrast to the tungsten and molybdenum bronzes having metallic conductivity, exhibits a semiconductor conductivity.¹²⁹

The reversible adsorption and removal of hydrogen occur also on heteropolyacids (HPA) and heteropolysalts formed from molybdenum and tungsten oxides. This process has been investigated by the temperature-programmed reduction (TPR) and IR spectroscopic methods in relation to the system $\text{H}_3\text{PMo}_{12-x}\text{W}_x\text{O}_{40} + \text{Pd/C}$.¹³⁰

It was found that H_2 is absorbed already at room temperature, while water is evolved at a higher temperature. At 300 °C, the absorption of H_2 and the exchange between H_2 and D_2 take place also in the absence of Pt. The process includes two stages: (1) rapid dissociation of H_2 with the initial formation of atoms and then H^+ ions, diffusing into the bulk of the HPA, and (2) slow interaction of H^+ with the O atoms in the bulk phase. The rate of oxidation of H_2 depends little on the specific surface of the HPA.

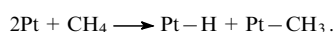
The salt $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$ exhibits an appreciably higher catalytic activity in the isomerisation of but-1-ene in the presence of hydrogen than the heteropolyacid $\text{H}_3\text{PW}_{12}\text{O}_{40}$.¹³¹ It was also found that the reactivity of the salt increases with increasing H_2 pressure, whereas that of the acid is independent of this parameter. Protons of two types have been detected in the system by NMR: some of them are manifested only in the presence of H_2 in the gas phase, whilst others are present at the surface of the salt also when the system is evacuated. The reversibly bound hydrogen is evidently formed on silver and then diffuses to the organic molecule and participates in catalysis.

The oxidation of methane to CO_2 and H_2O on the $\text{Pt/V}_2\text{O}_5$ catalyst with a very low Pt content (0.15%) has been investigated by scanning calorimetry *in situ*.^{132, 133} When $\text{Pt/V}_2\text{O}_5$ is heated to 550 °C, the stable V_2O_4 phase is formed, which can be detected from the heat of the reversible phase transition between the monoclinic and tetragonal forms of V_2O_4 , occurring at 68 °C. The stable phase proved to be completely inactive in catalysis at 275 °C.

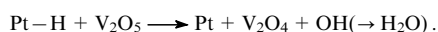
On the other hand, the reduction of the catalyst with methane at 275 °C leads to the formation of a metastable reduced vanadium oxide phase. Under these conditions, 20%–25% of oxygen is removed from the specimen and the effective stoichiometric formula of the oxide becomes close to V_2O_4 . However, the heat of the reversible transition from the monoclinic to the tetragonal form is not then observed. The stable catalytic activity of the metastable phase is retained when the specimen is cooled to 185 °C. The temperature of its reoxidation with oxygen is higher by almost 200 °C than for the stable phase. The low-temperature (50–350 °C) stage of the oxidation of the metastable phase is then characterised by an anomalously high heat of reaction ($\Delta H = 335\text{--}502\text{ kJ mol}^{-1}$). On heating, the metastable phase is converted into the stable phase with evolution of a large amount of heat.

The study of the $\text{Pt/V}_2\text{O}_5$ surface by the XPS method showed that vanadium atoms in the V, IV, and lower valence states are present after catalysis at the surfaces of both the stable (weakly active) and metastable (highly active) V_2O_5 phases. The surfaces of the active and inactive phases differ little in composition. As regards the state of Pt, according to XPS data the appearance of catalytic activity in $\text{Pt/V}_2\text{O}_5$ after heating in methane coincides in time with the disappearance of the oxidised forms of Pt (the binding energy is $4d_{5/2} = 317.1\text{ eV}$) and the appearance of metallic Pt (binding energy 314.1 eV).

Thus CH_4 dissociates on platinum particles in the course of its oxidation on the $\text{Pt/V}_2\text{O}_5$ catalyst.



Hydrogen atoms diffuse via the spillover mechanism to the V_2O_5 phase and reduce it to the nonequilibrium form V_2O_4 .



The nonequilibrium V_2O_4 phase facilitates the transport of oxygen to the $\text{Pt/V}_2\text{O}_5$ interface, in the vicinity of which methane is oxidised. The O_2 and CH_4 adsorption centres are probably separated.

Similar processes occur in the oxidation of hydrocarbons on the $\text{Pt/CeO}_2/\text{Al}_2\text{O}_3$ catalyst used in automobile catalytic converters.¹³⁴ Hydrogen is split off from the hydrocarbon being oxidised, diffuses into the bulk of CeO_2 , and reduces it to a lower oxide form. The reduction of CeO_2 in the Ni/CeO_2 system has been investigated in detail by the TPR, NMR, EPR, and IR spectroscopic methods.¹³⁵ At 400 °C, each gramme of CeO_2 is capable of absorbing up to 3.4×10^{20} hydrogen atoms ($\text{H/Ce} = 0.1$). This hydrogen hydrogenates isoprene at room temperature. Pure CeO_2 is inactive in hydrogenation, but the amount of hydrogen extracted by isoprene from the Ni/CeO_2 system is greater than would have been the case for the ratio $\text{H/Ni} = 1$. It is also possible that Ni^{2+} diffuses within the CeO_2 .

The results of experiments on the synthesis of methanol on a mixture of Cu/SiO_2 with ZnO/SiO_2 suggested that hydrogen diffuses from the Cu to the ZnO phase under the reaction conditions.¹³⁶ It is postulated that H atoms are formed on decomposition of the HCOO complex on Cu and migrate to ZnO, which serves as a reservoir for the reverse hydrogen spillover. According to IR spectroscopic data, ZnO is partly reduced in the course of the hydrogen spillover from Cu to ZnO.¹³⁷ The electrical conductivity of ZnO in its mixture with Cu increases under these conditions, which, according to Barrett *et al.*,¹³⁸ is associated with the intercalation of hydrogen and the formation of ZnOH_x . The diffusion of H atoms from the Cu to the ZnO phase has been demonstrated also by the direct neutron diffraction method.¹³⁹ A ZnO superlattice with an ordered arrangement of H atoms is then formed.

On the $\text{Cu/SiO}_2 + \text{ZnO/SiO}_2$ mixture, the yield of methanol from $\text{CO} + \text{H}_2$ was higher than on the separate components.¹⁴⁰ The authors explain such synergism by hydrogen spillover.

The study of the adsorption of hydrogen on the Cu/SiO_2 , Ru/SiO_2 , and Cu-Ru/SiO_2 catalysts led to the conclusion¹⁴¹ that atomic-like hydrogen participates in the spillover from Ru to Cu through SiO_2 .

TiO_2 is an effective hydrogen transferring agent. Its addition to the CuO-TiO_2 system greatly increases the activity and selectivity of the catalyst in the synthesis of methanol.¹⁴² The addition of Pd has the same effect.¹⁴³

Co^{2+} ions present in the NaY zeolite are reduced by hydrogen in the presence of Pd, provided that Co^{2+} and Pd^{2+} are in the same sodalite cavity.¹⁴⁴

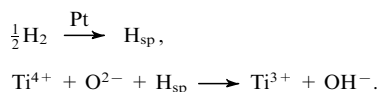
4. The strong metal – support interaction

The strong metal – support interaction (SMSI), inducing a change in the adsorption and catalytic properties of the carrier and the deposited metal, is as a rule observed in the reduction of an oxide carrier. This effect was named by Tauster and Fung,¹⁴⁵ who investigated the changes in the properties of TiO_2 on deposition of Pt. Under these conditions, the catalytic activity of the system in the Fischer – Tropsch synthesis is retained and even increases, although its adsorption capacity in relation to H_2 and CO falls.

The SMSI effect has been noted in the interaction of Pt, Pd, Ru, Rh, Ir, Ni Au, and Ag with TiO_2 , TiO , Ti_2O_3 , V_2O_5 , V_2O_3 , Ta_2O_5 , Nb_2O_5 , etc.⁵ The mechanism of the effect has been usually investigated in relation to the Pt/TiO_2 system. It is generally believed that the SMSI effect is induced by the reduction of the carrier as a result of the spillover of hydrogen from the metal to the carrier.

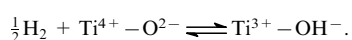
In certain cases, the SMSI is accompanied by the formation of alloys or intermetallic compounds. Convincing evidence for the formation of the Pt_3Ti phase in the high-temperature reduction of Pt/TiO_2 has been obtained.¹⁴⁶ An electron microscope study of the Pt/TiO_2 system showed that the spillover of hydrogen entails the partial coating of the deposited Pt with titanium oxide. At temperatures above 550 °C, TiO_2 is reduced to Ti_4O_7 . At a lower

temperature (300 °C), the formation of Ti^{3+} was observed.¹⁴⁷ The Ti^{3+} EPR signal vanishes on evacuation, but reappears after the admission of H_2 even at room temperature.

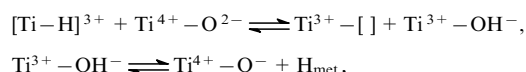


Thus at a low temperature the spillover results in the formation of the $\text{Ti}^{3+} + \text{OH}^-$ pair, whilst at high temperatures it gives rise to the bulk-phase reduction of the oxide.

In the spillover of hydrogen on Rh/TiO_2 , the amount of adsorbed hydrogen corresponded to the ratio $N_{\text{H}}/N_{\text{Rh}} = 3$. According to NMR data, Ti^{3+} centres participate in the diffusion of H atoms.¹⁴⁸ The adsorption of H_2 on Rh/TiO_2 (rutile) has been studied by the TPR, IR spectroscopic, EPR, and NMR methods,¹⁴⁹ showing that hydrogen is adsorbed at room temperature in two forms — strong and weak. The weak form participates in the reverse spillover and in the reduction of the support surface:



On anatase, such a process does not take place. The mechanism of hydrogen spillover is described by the following scheme:



where $[\]$ is a vacancy and H_{met} is metallised hydrogen. At 300 °C, hydrogen diffuses into the bulk of TiO_2 . Similar processes have been observed also on Pt/TiO_2 and Pd/TiO_2 .^{150, 151}

The valence state not only of the carrier but also of the metal may change as a result of the SMSI.¹⁵² In the Ni/TiO_2 system at 450 °C, large Ni particles interact with the carrier Ti^{3+} ions via spillover and the catalytic activity of such a two-phase system increases in the Fischer–Tropsch synthesis. However, at 650 °C a proportion of Ni migrates to the near-surface TiO_2 layers in the form of Ni^{n+} ions.

The increase in the electrical conductivity of TiO_2 in a hydrogen atmosphere after the deposition of Pt, Rh, or Ni was also accounted for by hydrogen spillover.^{153–155} An increase in electrical conductivity initially of the TiO_2 bound to Pt and then also of TiO_2 without Pt was observed in the $\text{Pt}/\text{TiO}_2 + \text{TiO}_2$ mixture in the presence of hydrogen. It is postulated that hydrogen diffuses to TiO_2 in the form of protons.

After heat treatment in hydrogen, the RhNb_2O_4 phase is formed in the $\text{Rh}/\text{SiO}_2 + \text{Nb}_2\text{O}_5$ system.¹⁵⁶ Hydrogen dissociates on Rh also after spillover to the Nb_2O_5 phase, reducing the latter.

When TiO_2 or Cr_2O_3 is added to the Rh/SiO_2 catalyst, the oxides partly ‘creep’ onto the Rh surface. According to TPR data, spillover hydrogen is adsorbed on the oxides and partly reduces them. With increase in the coverage of the rhodium surface by the oxides, the catalytic activity of the system in the hydrogenation of CO also increases.¹⁵⁷ It has been suggested that the dissociation of CO with participation of hydrogen takes place on an active centre incorporating Rh and a partly reduced titanium or chromium cation.

Ni/Mo_x catalysts, in which Ni is in the form of very small clusters (less than 2 nm) and the Ti, Zr, and Nb oxides are partly reduced, have been obtained by sputtering mixtures of a nickel salt with titanium, zirconium, or niobium salts.¹⁵⁰ The SMSI effect, occurring with participation of spillover hydrogen, has been observed in the formation of such catalysts. The catalysts obtained exhibit a high activity in the hydrogenation of CO_2 .

The SMSI effect has also been observed when Pt/TiO_2 was acted upon by hydrogen at 500 °C.¹⁵⁹ It has been suggested that a Pt–Ti alloy is formed in this system.

It has been demonstrated by the XPS method that heating of $\text{Ni}/\text{Al}_2\text{O}_3$ in a H_2 atmosphere leads to the SMSI, $(\text{Al}_x\text{O}_y)_n$ aggregates ‘creeping’ onto the surface of the deposited Ni.¹⁶⁰ Heating in O_2 or CO returns the metal to the initial state.

The coating of the catalyst by the carrier, accompanying the SMSI effect, has been noted in the interaction of methane with the $\text{MoO}_3 + \text{SiO}_2$, $\text{V}_2\text{O}_5 + \text{SiO}_2$, and $\text{Fe}_2\text{O}_3 + \text{SiO}_2$ systems subjected to a preliminary mechanochemical treatment.¹⁶¹ Electron microscope and electron diffraction studies have shown that, as a result of such treatment, the particles of the reduced oxides MoO_x and VO_y and also of metallic Fe are enclosed within a SiO_2 shell. It may be that the increased mobility of hydrogen in the mechanochemical treatment leads to the appearance of effects resembling SMSI.

5. Synergism in catalysis

The phenomenon of synergism, *i.e.* of the non additive increase in activity in mixtures of catalyst components, has been often investigated in relation to the hydrodesulfurisation process on the $\text{Co}(\text{Ni})\text{--Mo}(\text{W})$ catalyst. Delmon¹⁶² gave the first explanation of this phenomenon, postulating that the Co--Mo--S catalyst consists of two phases. According to the model of contact synergism which he proposed,^{163, 164} hydrogen is activated on the Co_9S_8 or NiS phase, while the sulfur compound being hydrogenated (for example, thiophene) is activated on the MoS_2 phase, hydrogen spillover occurring between the two phases. In a later model,¹⁶⁵ it was postulated that hydrogen spillover takes place between the CoS_2 and CoMoS phases.

The view that, whilst present in the real catalyst, the Co_9S_8 and NiS sulfide phases do not apparently play decisive roles in hydro-treating has predominated recently.^{166–176} The formation of a ‘ Co--Mo--S ’ phase, in which the Co atoms are located on the side faces or edges of MoS_2 microplates, has been observed by various physical methods (EXAFS, NMR, XRD phase analysis, *etc.*). The coordination number of Co is IV or V according to EXAFS data. Such an optimum ratio is attained when the Co atoms are located on the edges of MoS_2 microcrystallites.

Data obtained by Mössbauer spectroscopy^{177, 178} have shown that the same CoS species are formed under sulfiding conditions on the $\text{CoMo}/\text{Al}_2\text{O}_3$ catalyst as on $\text{Co}/\text{Al}_2\text{O}_3$, while on the CoMo/C catalyst the same CoS species are formed as on Co/C . This fact throws doubt on the hypothesis of the important role of the ‘ Co--Mo--S ’ phase. The MoS_2 phase is then regarded as a simple diluent. At the same time, it has been justly suggested that the CoMoS/C system may differ from $\text{CoMoS}/\text{Al}_2\text{O}_3$.¹⁶³ The Co/C catalyst exhibits an activity which is only three times lower than that of CoMoS/C .¹⁷⁹ The activities of the $\text{Co}/\text{Al}_2\text{O}_3$ and $\text{CoMoS}/\text{Al}_2\text{O}_3$ catalysts differ to a much greater extent.

As already mentioned, the Co atoms in the Co--Mo--S system are located on the edges of the MoS_2 microcrystallites.¹⁸⁰ The Co_9S_8 phase also exists, but its positive role is associated not with hydrogen spillover but with its additional function as a support for the Co--Mo--S phase.

The mechanism of the hydrodesulfurisation of thiophene on the $\text{Co}/\text{Al}_2\text{O}_3$, $\text{Mo}/\text{Al}_2\text{O}_3$, and $\text{CoMo}/\text{Al}_2\text{O}_3$ catalysts has been investigated by the TPD, TPR, and H–D exchange methods.¹⁸¹ On $\text{Mo}/\text{Al}_2\text{O}_3$ and $\text{CoMo}/\text{Al}_2\text{O}_3$, the TPR spectra of thiophene, tetrahydrothiophene and butanethiol proved to be very similar. At the same time, on the last catalyst the peaks due to the reaction products were displaced towards the region of low temperatures, which indicates higher rates of their formation. The TPR spectra of the same initial compounds on $\text{Co}/\text{Al}_2\text{O}_3$ differed sharply: no peaks corresponding to the majority of the main reaction products were observed on them. In contrast to $\text{Mo}/\text{Al}_2\text{O}_3$, hydrogen was present on the $\text{Co}/\text{Al}_2\text{O}_3$ and $\text{CoMo}/\text{Al}_2\text{O}_3$ surfaces in a weakly bound form.

The results obtained confirmed the view that thiophene (or its derivatives) are adsorbed on the MoS_2 anionic vacancies while hydrogen is activated on cobalt sulfide. Hydrogen may be transferred by means of spillover if the Mo and Co centres belong to different phases or via migration if these centres form part of the composition of a single phase. Presumably the hydrogenation–dehydrogenation reactions occur on centres of one type, whilst desulfurisation takes place on centres of another type.

Much interest has been shown recently in solid superacids of the type of $\text{ZrO}_2\text{--SO}_4^{2-}$, capable of catalysing a series of most important organic reactions of the acid type. The addition of Pt may improve the catalytic properties of superacids and, in particular, may increase their resistance to poisoning by coke, since the latter is hydrogenated by the spillover hydrogen.^{182–184} Analysis of the IR spectra showed that new proton centres are formed in place of the acid Lewis centres under these conditions. Molecular hydrogen dissociates on Pt and the H atoms formed migrate via spillover to $\text{ZrO}_2\text{--SO}_4^{2-}$. It has been suggested that the H atom gives up an electron on Lewis centres, being converted into a H^+ ion, which is stabilised by the nearest surface O^{2-} ion. The rate of the skeletal isomerisation of butane on such a catalyst is much higher than on the $\text{ZrO}_2\text{--SO}_4^{2-}$ catalyst without Pt.

The hydrogenation of CH_3OH , $(\text{CH}_3)_2\text{O}$, $\text{C}_2\text{H}_5\text{OH}$, $\text{C}_3\text{H}_7\text{OH}$ and HCOOH on the $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst has been investigated by the TPR method.¹⁸⁵ It was found that the rate of formation of methane from all five compounds is the same and close to the rate of hydrogenation of the CH_2O fragment formed from the adsorbed CO and H_2 . Thus in all cases hydrogenation has the same rate-limiting stage, which may be the spillover of hydrogen from Ni to the organic molecule adsorbed on Al_2O_3 .

In the hydrogenation of CO on $\text{Ni}/\text{Al}_2\text{O}_3$ mixed with Pt/SiO_2 (or $\text{Ru}/\text{Al}_2\text{O}_3$), carbon monoxide is adsorbed on Pt, while hydrogen migrates via the spillover mechanism from Ni to Al_2O_3 .¹⁸⁶ Data obtained by the TPD method have shown that the products are desorbed from the H_2CO complex. In the absence of the second component, such a complex is not formed on Pt/SiO_2 . The independence of the rate of its formation of the Ni concentration indicates the formation of this complex on the support.

The H_2CO complex was also detected by the TPR method in the conversion of CO into methane on the $\text{Ni}/\text{SiO}_2 + \text{Al}_2\text{O}_3$ mixture.¹⁸⁷ The rate of spillover increased with improvement of the contact between the particles and with increase in the nickel concentration.

VI. Conclusion

Thus the phenomenon of hydrogen spillover, common in heterogeneous catalysis, has been observed mainly in multiphase systems. Hydrogen is activated on one of the phases, frequently the metallic phase (although this may occur also on certain transition metal oxide or sulfide phases) and then diffuses to the other phase, which in the absence of the activator phase is inactive or its activity is low in relation to the adsorption of hydrogen. The spillover hydrogen on the second phase may be detected by physical methods (EPR, NMR, neutron diffraction, etc.) and also from the change in the properties of the phase (for example, as a result of the reduction of oxides) or by virtue of the manifestation of new catalytic properties by the heterogeneous system.

The spillover phenomenon is not only of theoretical but also of considerable practical importance. The elucidation of the nature and rules governing spillover may promote a rational solution of the problem of the construction of multiphase catalysts. For this purpose, information is needed about the adsorption properties of each phase and also about the characteristic features of the interphase diffusion of hydrogen and its diffusion along individual phases. It appears that in catalysis different reactants are frequently activated on different phases and the catalytic reaction is effected as a result of interphase diffusion. It has been shown^{19,188} that the high activity and selectivity of multiphase oxide catalysts in oxidation reactions can be explained precisely by the occurrence of individual stages on different phases and by the diffusion (spillover) of oxygen between the phases.

This claim is probably even more valid in relation to catalytic reactions with participation of hydrogen. Hydrogen atoms or ions are more mobile than oxygen and may diffuse more easily. The so called 'bifunctional' catalyst, consisting of the supported metal, on which hydrogen is activated, and an oxide (frequently with distinct acid properties — for example Al_2O_3 and zeolites),

adsorbing or activating the component to be hydrogenated are widely used in catalytic reactions involving hydrogen. The role of interphase diffusion in such systems has been examined by Weisz.¹⁸⁹ Hydrogen spillover plays an important role in catalytic processes such as reforming, hydrogenation of unsaturated compounds, synthesis of methanol, isomerisation of hydrocarbons, and hydrodesulfurisation.

The mechanism of the hydrodesulfurisation reaction on the CoMo, NiMo, or NiW sulfide catalysts has been vigorously discussed in the literature. On the one hand, fairly numerous data indicate that multiphase catalysts are needed for the occurrence of this reaction. On the other hand, the idea that this requires not so much a multiphase system as the presence of centres with nonidentical functions, which can in general enter into the composition of the same phase, has been expressed recently with increasing frequency. However, in any variant it is essential to know the mechanism of the transport of hydrogen (or other adsorbed species) between such centres.

There is as yet no unanimous view about the mechanism of hydrogen spillover. The majority of investigators postulate that the initial stage of the spillover is homolytic dissociation of hydrogen on the metal phase (or an oxide or sulfide). However, the question in what form and by what mechanism hydrogen atoms pass from one phase to another remains controversial. It has been suggested that surface diffusion of the adsorbed species predominates, but in certain individual instances diffusion through the gas phase is not ruled out. The considerable scatter of hydrogen diffusion coefficients in spillover on various catalysts apparently indicates the diversity of the nature of the diffusing species and spillover mechanisms.

The nature of the hydrogen acceptor centres on the surfaces of oxides has been little investigated. It was indicated above that the number of hydrogen acceptor centres is as a rule small (usually less than 1% of the total number of surface sites). In this case, the question arises what role is played in spillover by the remaining centres, such as O^{2-} ions or OH groups. What is the ratio of the heats of adsorption of spillover hydrogen on the activator and on the acceptor centres? How do the kinetics of the reactions change in the course of the migration or spillover of adsorbed species of one or several types?

These and many other questions concerning the spillover mechanism have so far not been analysed in depth either theoretically or experimentally.

Further detailed investigations of spillover with quantitative estimation of factors such as diffusion coefficients, the number of spillover initiator and acceptor centres, and the bond energies between hydrogen and these centres are needed.

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Azafluorenes. Synthesis and conversions

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Abstract. Data on the chemistry of azafluorenes (indeno[1,2-b]pyridines) for the last two decades are summarised. Methods of synthesis of all isomeric (as regards the position of the nitrogen atom) azafluorenes are considered. The main reactions of azafluorenes are analysed, their reactivity is determined by the presence and mutual influence of two different conjugated fused rings (benzene and pyridine) and the mode of fusion of the indene and pyridine fragments. The principal conversions of substituents at different positions of the azafluorene system are considered. Evidence is presented on the natural occurrence of azafluorenes, the biological activity of their synthetic derivatives, and on the structure and physicochemical properties of azafluorenes and their derivatives. The bibliography includes 204 references.

I. Introduction

The chemistry of isomeric azafluorenes (indeno[1,2-b]pyridines) has been discussed in two reviews,^{1,2} which summarise the data published mostly before 1975. It should be noted that these reviews dealt mainly with the chemistry of 2-azafluorene, and an extreme scarcity of data on isomeric 1- and 3-azafluorenes has been mentioned (1-azafluorene was first obtained as late as 1975). A large body of evidence has been accumulated in the current literature over the last two decades concerning the development of general methods of synthesis of these tricyclic fused systems together with in-depth analysis and comparison of reactivity of isomeric azafluorenes, and a search for promising biologically active derivatives among newly synthesised compounds. Considerable recent interest in azafluorenes has been stimulated by the discovery in mid-1980s of numerous plant alkaloids having mostly the structure of 4-azafluorenone. Moreover, there is evidence in both scientific and patent literature on the manifestation of antihistamine, neurotropic, antibacterial, antioxidant, and pesticide activities by azafluorene derivatives.

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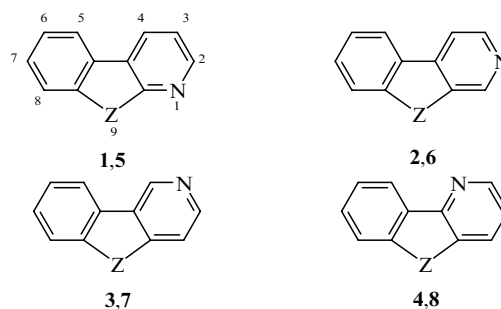
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This review presents and discusses the data on the strategy of synthesis of azafluorenes and their conversions involving the benzene, pyridine, and cyclopentadiene rings, which constitute the azafluorene system and exert a mutual influence on the chemical properties of these compounds. Data on the natural occurrence of azafluorenes and the biological activity of their synthetic derivatives are also generalised.

II. Structure and physicochemical properties

All of the isomeric (as regards the position of the nitrogen atom) unsubstituted azafluorenes (**1–4**) and azafluorenones (**5–8**)^{1–4} the structure of which is given below, have now been described:



1–4: Z = CH₂; **5–8:** Z = C=O.

Quantum-chemical calculations have been performed^{5,6} for the distribution of π -electron density and localisation energy of the protonated forms of 1-, 3-, and 4-azafluorenones. According to these calculations, electrophilic substitution must occur at the phenylene ring, presumably, at C(7). The luminescence spectra of unsubstituted azafluorenes, their 9-oxo-derivatives, and 9-arylidenes azafluorenes have been studied.^{7–9} Thus, the UV spectra of 1- and 4-azafluorenes display a bathochromic shift of the α^* -absorption band, a hypsochromic shift of the p -band, and an increase in intensity of the α^* -band as compared with fluorene. In the case of 2-azafluorene, a hypsochromic shift of these bands is accompanied by a decrease in their intensity and a bathochromic shift of the α -band occurs. It is concluded that the α^* - and p -bands for 1- and 4-azafluorenes, like for fluorene, possess fluorescent character, while in the case of 2-azafluorene, this property is inherent in the α -band. Unlike other isomeric azafluorenes, 3-azafluorene is unstable and undergoes rapid photoconversions in the light.

The ^{13}C and ^1H NMR spectra of azafluorenes **1–4** have been studied.^{3, 10–12} The ^1H NMR spectra of a series of 9-arylidene-2-azafluorenes were also studied with the use of shift-reagents.⁸

The IR spectra of azafluorenes do not contain specific absorption bands and are mostly used in studies on the synthesis of derivatives of these compounds to confirm the presence and position of substituents. The carbonyl group in the azafluorene-9-ones **5–8** absorbs in the characteristic region, i.e., at $1715\text{--}1735\text{ cm}^{-1}$. The IR spectra of 1,4-dihydro-4-azafluorenes,¹³ particularly those containing electron-withdrawing substituents at C(3), were studied in more detail.^{14, 15}

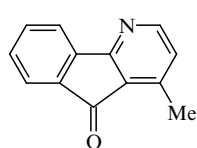
X-Ray analysis of 1,3,9-triphenyl-4-azafluorene have shown that the torsional angles between the planes of the azafluorene and phenyl rings are equal to 8.4° , 55.4° , and 44° , respectively.¹⁶ According to the X-ray data, the azafluorene polycycle of 9-benzylidene-1-azafluorene is not absolutely flat, since the angle between its two six-membered rings is 4.1° .¹⁷ The exocyclic carbon atom, C(10), of the fulvene fragment is above the plane of the five-membered ring, the corresponding torsional angle is 4° . The carbon atom of the phenyl substituent bound to C₁₀ deviates from the plane of the five-membered ring even more, the corresponding torsional angle is as much as 8.5° . The phenyl substituent is turned by 65° relative to the mean plane of the azafluorene skeleton, which confirms that through-space charge-transfer complexes can form in the case where the nitrogen atom occupies position 1 in the azafluorene fragment.¹⁸

There are no quantitative data on the basicity of the pyridine fragment and the CH-acidity of the methylene group of azafluorenes. The quantum-chemical characteristics of alkyl- and nitro-substituted 4-azafluorenones have been considered.¹⁹

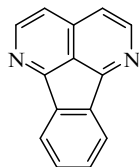
A systematic study of the electron impact-induced mass spectra of azafluorenes and their derivatives has been carried out.^{3, 20–28} It has been shown that fragmentation of the unsubstituted azafluorenes **1–4** is virtually independent of the position of the nitrogen atom. The mass spectra of these compounds contain molecular ions as the most abundant peaks, while the characteristic pathways of their fragmentation are determined by the mode of elimination of the hydrogen atom and the HCN molecule. Fragmentation of the azafluorenones **5–8** is characterised by the elimination of the CO molecule, which is most intense for 1- and 4-azafluorenones. In the case of substituted azafluorenones, the character of fragmentation is determined by the nature of the substituent. Quantum-chemical calculations were used to estimate the probability of electron impact-induced rearrangement of azafluorenes and their derivatives.²⁷

III. Occurrence in nature

The first plant alkaloid with the azafluorene structure was isolated in 1976 from the arboreal part of the plant *Onychopetalum amazonicum*.²⁹ This alkaloid (onychin, **9**) was initially identified as 4-methyl-1-azafluoren-9-one. However, the synthesis of the isomeric ketones³⁰ has established that onychin is in fact 1-methyl-4-azafluoren-9-one. The ^1H and ^{13}C NMR spectra of this alkaloid have been studied in detail.³¹



9, Onychin



10, Eupolauridine

Recent studies of the plants of the Annonaceae genus have revealed 14 alkaloids having the structure of methoxy- and hydroxy-substituted 4-azafluorenones;^{32–35} methods for the synthesis of some of these compounds have been proposed.^{36–45} Several alkaloids of more complex structure also incorporate azafluorenes as fragments, cf., e.g., eupolauridine (**10**).⁴⁶ It should

be noted that 4-azafluorene was first isolated from tarry coal coking products;⁴⁷ some of its derivatives have been recently identified by chromatographic methods in the atmosphere in the vicinity of coal-tar chemical plants.⁴⁸

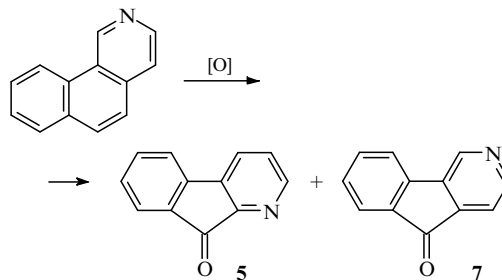
IV. Methods of azafluorene synthesis

The known methods of azafluorene synthesis can be divided into three main groups. The first of them makes use of degradation of nitrogen-containing fused compounds into tricyclic azafluorenes. The principle exploited in the second group is the increase in the number of fused rings by annelation of the heterocycle to the bicyclic system (indene). The strategy of the third group methods entails various reactions of intramolecular cyclocondensation of aryl- or aroyl pyridines with involvement of substituents.

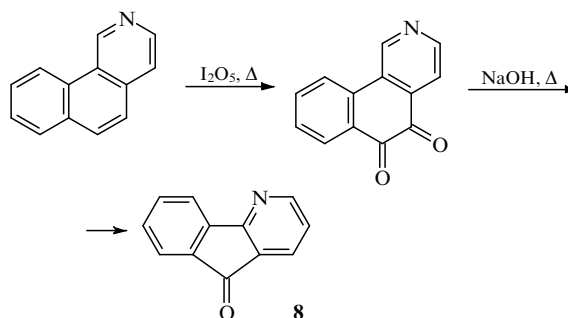
1. Oxidative degradation of azafluoranthrenes and azaphenanthrenes

The first 1- and 4-azafluorenones derivatives were obtained by oxidation of substituted azaphenanthrenes with potassium permanganate.^{49, 50}

Similarly, several azafluoranthrenes were converted with low yields into these azafluorenones.^{51, 52} Later,³ the 1- and 3-azafluorenones **5** and **7** were isolated with a total yield of 12% from the products of oxidation of 2-azaphenanthrene with potassium permanganate.



An effective two-step procedure has been proposed for the synthesis of 1- and 4-azafluorenones by oxidation of the corresponding azaphenanthrenes azaphenanthrenequinones (yields 48%–80%) with iodine pentoxide.⁵³ They smoothly rearrange into azafluorenones (yields 70%–88%) on heating in aqueous solution of alkali. The limitation of this method is that some of the original azaphenanthrenes are difficult to obtain. For example, 2-azaphenanthrene is obtained from 2-formylnaphthalene in four steps.

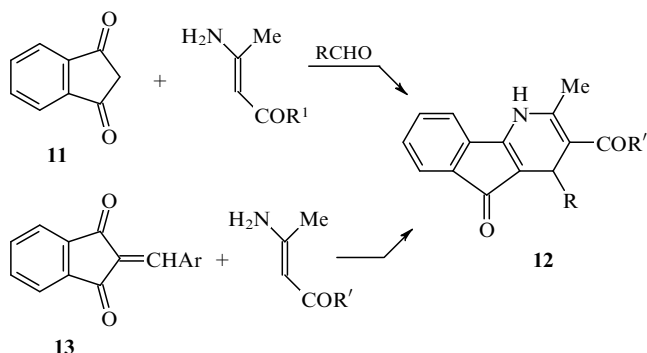


2. Condensations involving indane derivatives

The strategy of formation of azafluorene systems based on the indane derivatives entails several approaches differing in the number of components used, the source of nitrogen needed for the formation of the heterocycle (ammonia, β -aminocrotonates, β -aminoalkanoic acids, amino- or alkylamino-derivatives of indane) and, finally, the type of heterocyclocondensation.

The condensation in a three-component system, indane-1,3-dione (**11**)–aminocrotonate–aldehyde, is the most efficient and

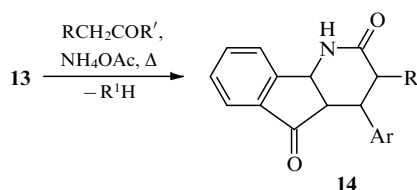
widely used for the synthesis of 1,4-dihydro-4-azafluorenes.^{54–59} The resulting dihydroazafluorenes (**12**) can be then easily aromatised with oxidants or, in some cases, under UV irradiation.^{60–63}



R = H, Me, Ar; R' = OMe, OEt, SMe, SEt, SCH₂Ph.

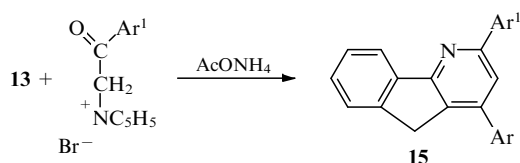
Apparently, the first step is the reaction of the aldehyde with the activated methylene group of the indane-1,3-dione **11** resulting in the intermediate 2-arylidene-(or 2-alkylidene)indanedione. The latter must be then converted into the polycycle **12** as a result of [3 + 3]-cyclocondensation. Indeed, this pathway has been confirmed experimentally^{64–69} for the condensation in a two-component system: arylidenediones (**13**)–aminocrotonates.

If ammonia and esters (or amides) containing an activated α -methylene group are used in condensation with arylidenediones, the hexahydro derivatives of 4-azafluorene-3,9-diones (**14**) are formed with yields of up to 80%.

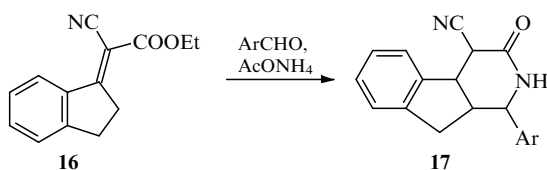


R = CN, COOEt, COOMe, COOPh; R' = OEt, NH₂;
Ar = Ph, C₆H₄Cl-4, C₆H₄Me-4.

By varying the methylene component, fully aromatised azafluorenes can be obtained in this condensation. Thus, in the reaction of the arylidenedione **13** with 1-phenacylpyridinium bromide the good leaving azinium group favours the formation of the aromatic indenopyridinium structure **15**.^{55,70} This procedure was used in the synthesis of many 1,3-diaryl-4-azafluorenes **15**.



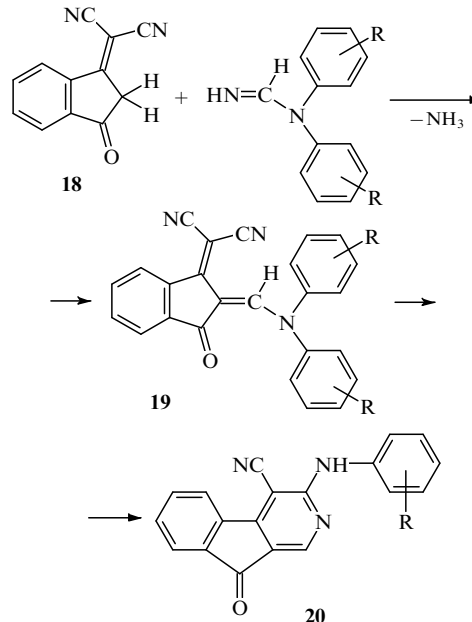
On going from indanones to the indanylidenes **16**, as components of the condensation with aldehydes and ammonia, one can obtain substituted azafluorenes **17**, e.g., cyanohexahydro-2-azafluorene-3-one.⁶⁸



Ar = Ph, C₆H₄NO₂-4.

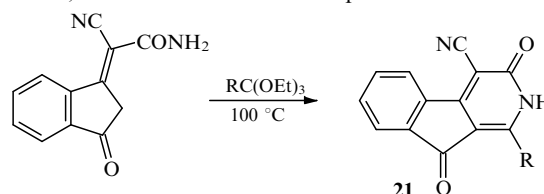
The use of nitrogen-containing components in the form of nitriles, amines, or amides has made it possible to pass to the condensation of two-component systems.

3-Dicyanomethyleneindanone (**18**) possessing an active methylene group forms upon interaction with diarylformamidines the derivatives **19**, which further convert into 3-arylamino-substituted 2-azafluorene-9-ones **20** as a result of cyclisation and Dimroth rearrangement.⁷¹



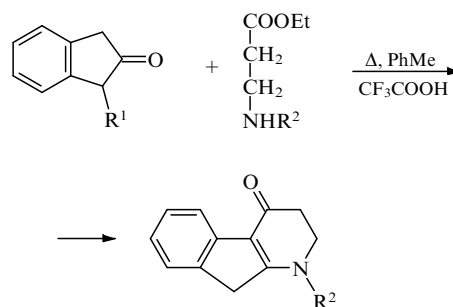
R = H, 2-Me, 2-Cl, 2-Pr, 2-MeO, 4-Me, etc.

2,3-Dihydroxy-2-azafluorene-3-one derivatives **21** can be obtained by heating (3-oxoindanylidene) cyanoacetamide with orthoesters.⁷² The stage of intramolecular heterocyclisation must be preceded by condensation with the formation of 2-methyleneindanone, with the same substitution pattern.



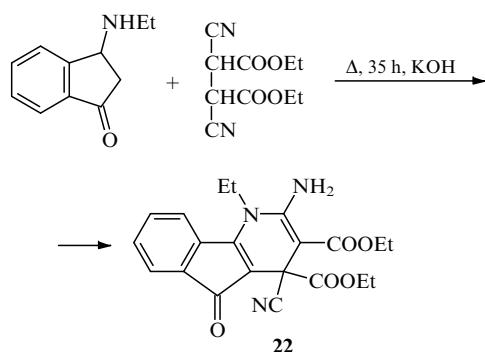
R = H, Me, Ph.

2-Indanones enter into [2 + 4]-cyclocondensation on heating with ethyl 2-benzyl- or 3-methylaminopropionate to give high yields of tetrahydro-1-azafluorene-4-ones.^{73,74}

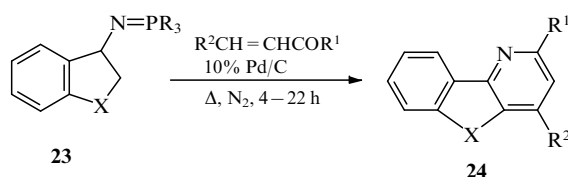


R¹ = H, Ph; R² = Me, CH₂Ph.

The amino group initially introduced into the C(3) position of indan-1-one allows the construction of 4-azafluorenes with the dihydropyridine ring (**22**). These indanone derivatives enter into [3 + 3]-cyclocondensation, e.g., with diethyl dicyanosuccinate.⁷⁵

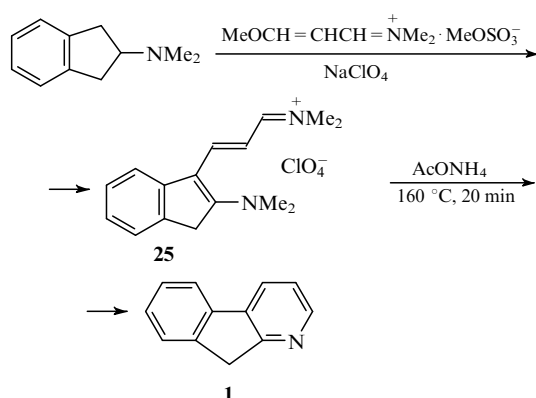


[3 + 3]-Heterocyclisation occurs in the case of iminophosphoranes **23** and α,β -unsaturated ketones or aldehydes. This gives in the aromatic 4-azafluorenes **24**.⁷⁶

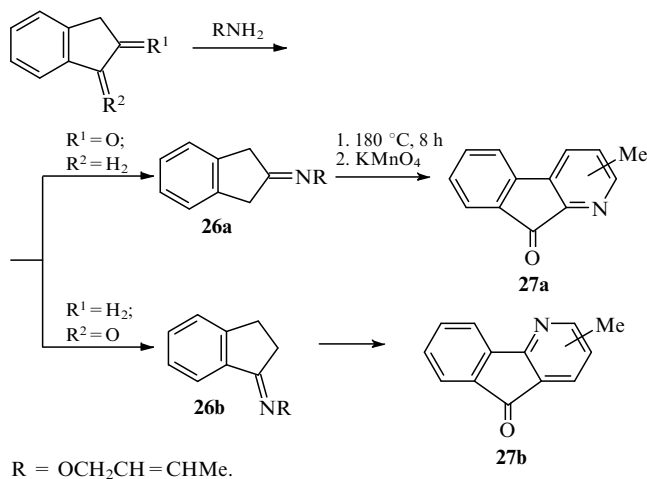


R = Buⁿ, Ph; X = CH₂, CO;
R¹, R² = H, Me, Ph.

Several intramolecular cyclisations of one-component systems are known. 1-Azafluorene (**1**) was obtained by thermal cyclisation of the polymethinium salt of 2-dimethylaminoindene (**25**) in the presence of ammonium acetate.⁴



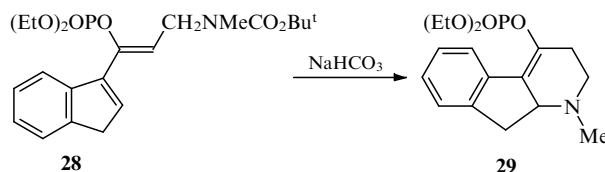
The isomers of the alkaloid onychin (**9**), two methyl-substituted 1-azafluorenones and two methyl-substituted 4-azafluorenones, were obtained by oxidative thermolysis of 1(2)-but-2-enyloxyiminoindanes **26**.³⁰ In the former case, a mixture of



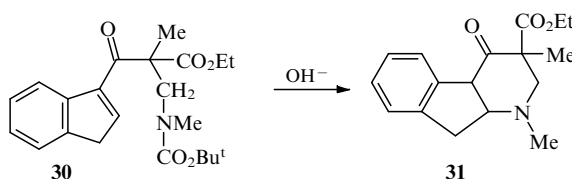
R = OCH₂CH=CHMe.

4- and 2-methyl-1-azafluorenes (**27a**) was formed from the 2-substituted derivative **26a** in a 38% yield; in the latter, a mixture of 1- and 3-methyl-4-azafluorenes (**27b**) was formed from the 1-substituted derivative **26b**.

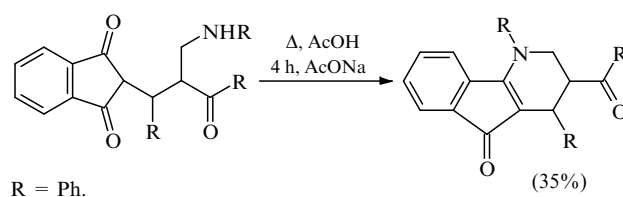
The dienol phosphate **28** is converted into the tetrahydro-1-azafluorene **29** under the action of sodium hydrogen-carbonate.^{77, 78}



An analogous electrophilic cyclisation was used to convert the β -keto ester **30** into the substituted hexahydro-1-azafluorene (**31**).⁷⁹

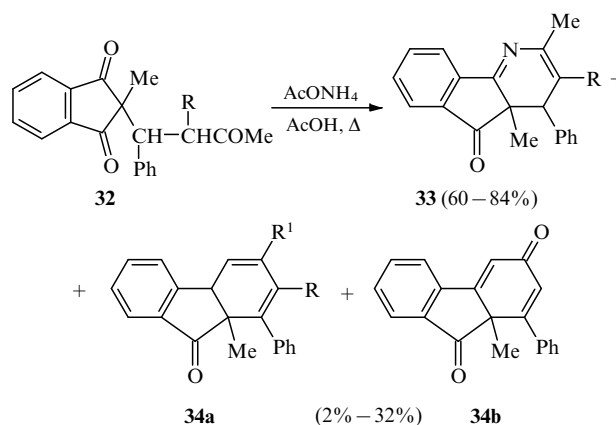


Azafluorene systems can be formed by intramolecular heterocyclisation of indan-1(3)-ones with 3-phenylamino substituents at C(2).⁸⁰ This procedure was used to obtain partially hydrogenated 4-azafluorenones from 1-indane-1,3-diones having an α -amino-methyl-substituted fragment of propiophenone at C(2).



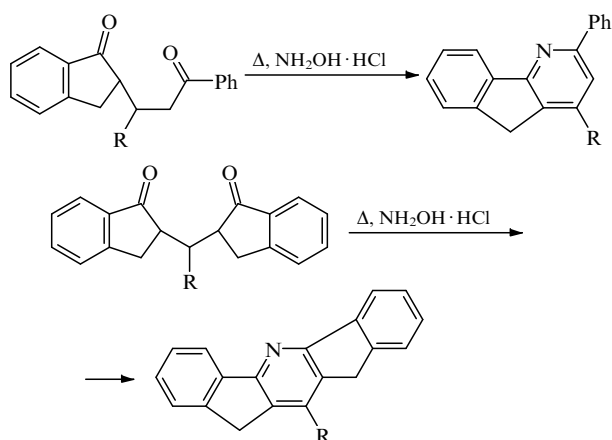
R = Ph.

1,5-Diketones smoothly form a pyridine ring in reactions with primary amines; therefore, the principle of heterocyclisation has been successfully applied to the synthesis of azafluorenes. Thus, cyclisation of 2-(3'-oxoalkyl)-substituted indanediones (**32**) has been used to synthesise dihydro derivatives of 4-azafluorenone **33** with yields of up to 84%.⁸¹ In this case, the formation of azafluorenes is accompanied by cyclisation into the substituted dihydrofluorenones **34**, which is suppressed in aprotic solvents. When the methyl group at C(2) of indanone is substituted for bromine, the azafluorene system is not formed at all.



R = CO₂Et, COMe; R¹ = OH, NH₂

Boiling of 2-(3-oxo-3-phenylpropyl)indan-1-one^{82, 83} or bis-(1-oxoindan-2-yl)methanes in ethanol with a twofold excess of $\text{NH}_2\text{OH} \cdot \text{HCl}$ results in 4-azafluorenes or indene[1,2-*b*]azafluorenes.⁸²

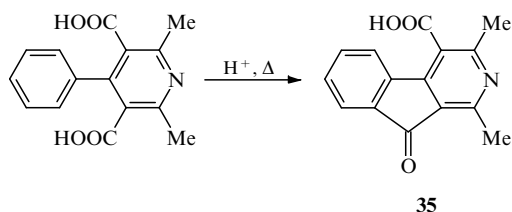


$R = \text{H, Me, Ph.}$

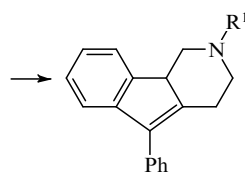
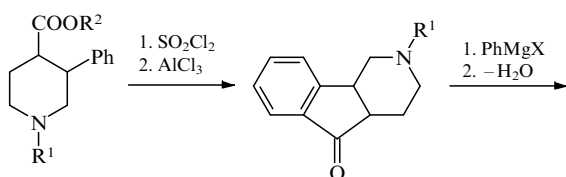
Until now, compounds of the 3-azafluorene series could not be obtained from indanone derivatives. Despite successful application of the approach discussed to the synthesis of some derivatives of 1- and 2-azafluorenes, this procedure seems to be of preparative importance in the synthesis of 4-azafluorene derivatives.

3. Intramolecular condensations of substituted aryl- and benzoylpyridines

The availability of diverse pyridine derivatives has offered broad possibilities for synthesising all isomeric azafluorenes based on them and varying the nature and position of substituents. The methods considered in this section are mostly based on cyclisation of aryl- or aroylpyridines with benzene or pyridine rings substituted in the ortho-position. The pioneering study of this kind,⁸⁴ which was followed by numerous analogous investigations,^{45, 52, 85–87} reported on the acid-catalysed cyclisation of 2,6-dimethyl-4-phenylpyridine-3,5-dicarboxylic acid to the azafluorenone 35.

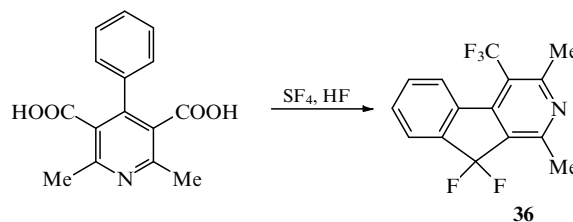


Analogous cyclisation of the corresponding phenylpyridine-carboxylic acids,^{85–88} respective acid chlorides,⁸⁹ nitriles and esters,^{45, 46, 90–92} resulted in a vast number of 2- and 4-azafluorene derivatives. Sulfuric⁸⁴ and polyphosphoric acids,^{45, 92–94} aluminium chloride,⁹⁵ and some other compounds⁹⁶ were used as condensing agents. Thus, 3-azafluorene derivatives have been obtained from phenylpiperidinic acids by converting them into acid chlorides followed by cyclisation in the presence of AlCl_3 .⁹⁵

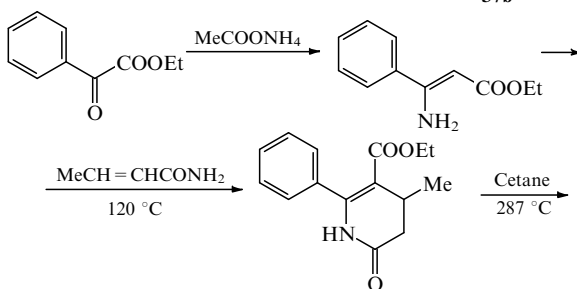
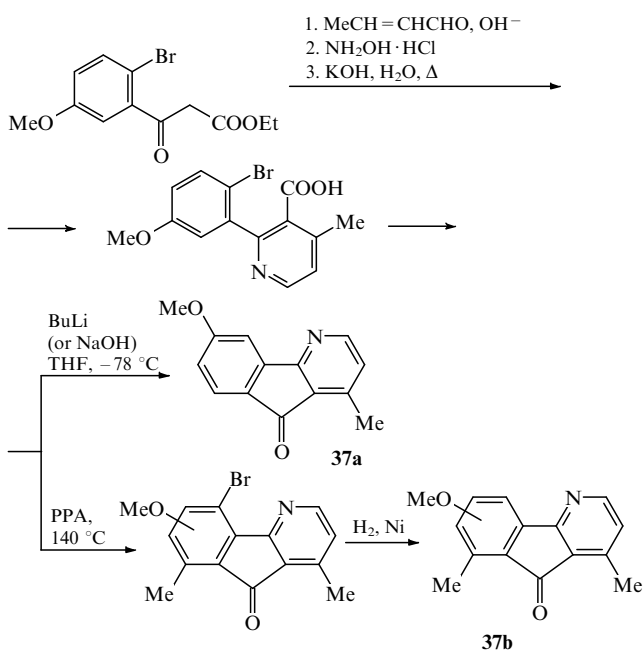


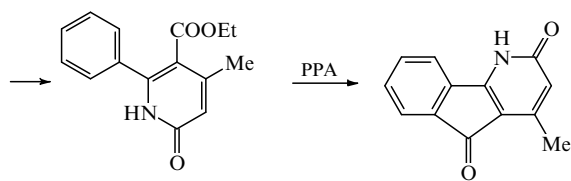
$R^1 = \text{Me, CH}_2\text{Ph; } R^2 = \text{H, Me, Et.}$

The cyclisation of 4-phenylpyridine-3,5-dicarboxylic acid in the presence of hydrofluoric acid is worth noting.⁹⁵ This reaction gives 9,9-difluoro-1,3-dimethyl-4-trifluoromethyl-2-azafluorene 36 instead of the expected azafluorene-9-one with a carboxylic group at C(4).



Methods have been proposed for synthesising the azafluorene alkaloids 37a,b^{41, 45} and 38³⁵ by cyclisation of the corresponding pyridine derivatives, which had been prepared from benzoylacetates as shown in the schemes given below. It has been found that the alkaloid 37b possesses antifungal activity.⁹³

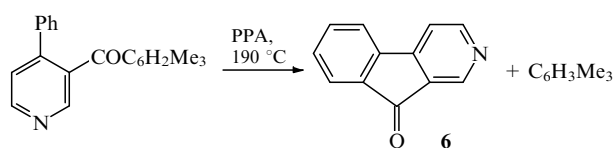




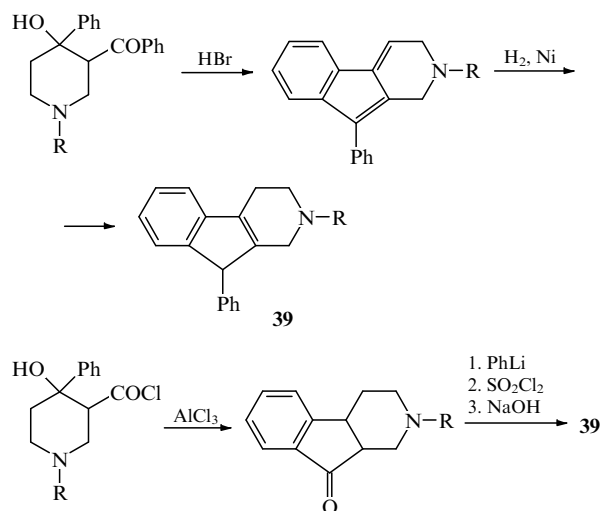
PPA = polyphosphoric acid.

Synthesis of azafluorenes by thermal cyclocondensation of pyridinecarboxylic acids has the following limitations: multi-stage of synthesis of the starting compounds and, in the case of 1- and 3-azafluorenone derivatives (the former has not been prepared by this method thus far), the high probability of a side-process, decarboxylation of derivatives of α - and β -pyridinecarboxylic acids.

Substituted phenylpyridines having an aroyl group in the ortho-position can also be used in the acid-catalysed thermal cyclisation.^{3, 96, 97}

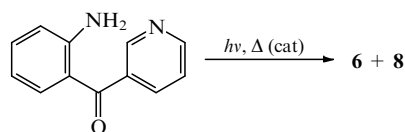


Similar cyclisations occur successfully in the case of piperidine derivatives. For example, a number of 9-phenyl-tetrahydro-2-azafluorenes have been obtained, one of which (**39**, R = Me) is used as an antihistamine drug.^{89, 98–101}

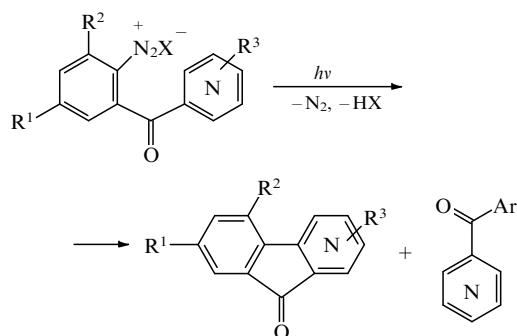


R = Alk, Ph.

The *o*-amino group served as a leaving group in the radical intramolecular cyclisation of 3-benzoylpyridine.^{102, 103} UV-irradiation or heating of 3-(2-aminobenzoyl)pyridine in the presence of copper, silver, zinc, or iron gives a mixture of 4- and 2-azafluorenones (**6** and **8**) in approximately equal amounts (total yield 50%–60%).



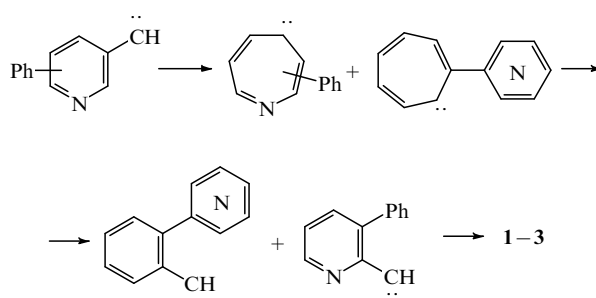
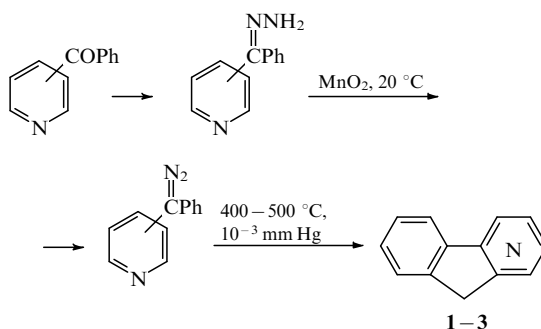
A series of 2-, 3-, and 4-azafluorenones substituted in the benzene or pyridine ring have been synthesised by photochemical decomposition of diazonium salts obtained from *o*-aminobenzoyl derivatives of pyridine.¹⁰⁴



R¹, R², R³ = H, Me, F, Cl.

The yield of azafluorenones varied from 25% to 74% depending on the nature of substituents, concentration of diazonium ions and reaction sensitisers (2,2'-dipyridyl complexes with ruthenium or copper). With sensitisers, the formation of benzoylketones as by-products decreased sharply. Radical cyclisation to azafluorenones when the diazonium ion is localised in the pyridine ring (particularly, in the α -position), is less effective. This method can be considered as general, although it has a number of disadvantages, such as the multi-stage synthesis of the starting compounds and the non-selectivity of the cyclisation step characteristic of radical processes.

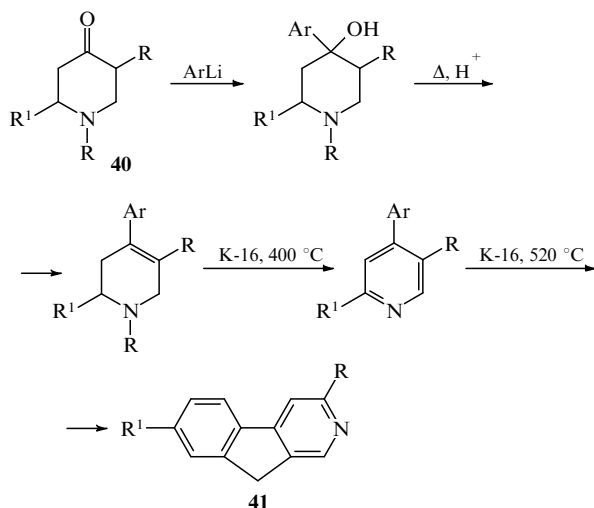
Wentrup *et al.*^{3, 105} have carried out an original conversion of 3- and 4-benzoylpyridines into azafluorenes via hydrazones and diazomethanes, which were subjected to thermolysis *in vacuo*. Under pyrolysis conditions, as was demonstrated in experiments with radiolabelled carbon atoms,^{3, 106} the carbenes formed result in expansion of the benzene and/or pyridine ring with subsequent cyclisation to azafluorenes.



In the case of phenyl-3-pyridyldiazomethane, a 1.3 : 1.0 mixture of 1- and 3-azafluorenes is formed in a total yield of 42%, while the pyrolysis of 4-pyridyl-substituted diazomethane gives only 2-azafluorene (68% yield). 4-Azafluorene cannot be obtained by this route.

Serious drawbacks of this method (multi-stage synthesis, the formation of mixtures of azafluorenes, and the necessity to perform pyrolysis in high vacuum) do not allow its use for preparative purposes.

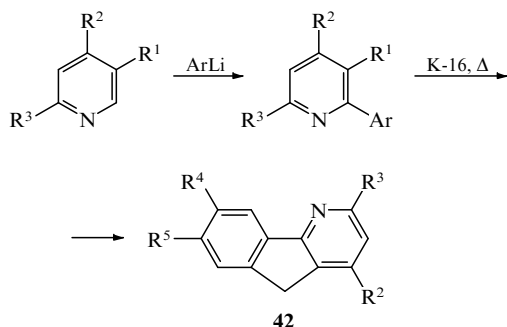
A general procedure for the preparative synthesis of all isomeric azafluorenes (including alkyl- and aryl-substituted ones) has been developed in our laboratory.^{107–115} The number of stages in this method depends on the procedure used for obtaining the synthon with a predetermined position of substituents.^{109–118} At the final stage, the azafluorene precursor, viz., the alkyl-substituted phenylpyridine, is subjected to vapour-phase heterocyclisation at 520–540 °C on an industrial catalyst K-16 (a mixture of metal oxides). With 1,2,5-trimethyl-4-piperidone **40** as the starting material, 3-methyl-2-azafluorene **41** was obtained by this method;¹⁰⁸ some other 2-, 3- and 4-azafluorenes with different positions of methyl and phenyl substituents were also obtained.^{109, 112–115}



R = Me; R¹ = H, Me; Ar = Ph, C₆H₄Me-4, C₆H₃Me₂-2,4.

However, the attempts to obtain 1-azafluorene derivatives from the corresponding γ -piperidones have so far been unsuccessful.

A two-stage synthesis of 4-azafluorene derivatives **42** consisting in nucleophilic arylation of pyridine, 3-picoline, and lutidines with subsequent heterocatalytic dehydrocyclisation of alkylphenylpyridines is highly efficient.^{109, 116}

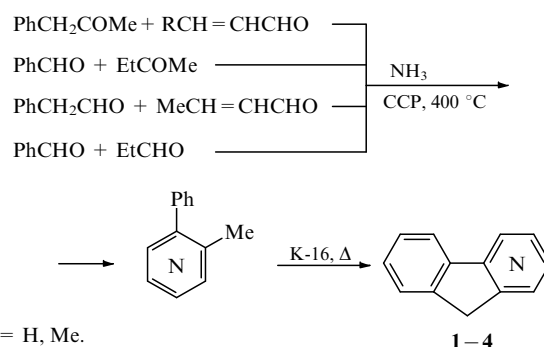


R¹–R⁵ = H, Me; Ar = Ph, C₆H₄Me-2, C₆H₄Me-4, C₆H₃Me₂-3,4.

Dehydrocyclisation of 3-methyl-2-phenylpyridine or 2-*o*-tolylpyridine gives 4-azafluorene with equal yields (~20%) irrespective of what ring, pyridine or benzene, is involved in ring closure with involvement of the methyl group. However, this two-stage modification does not permit one to obtain azafluorenes with any other position of the nitrogen atom.

The most common approach is the one, in which all the necessary methyl(phenyl)-substituted pyridines are synthesised by the Chichibabin method (with yields of up to 55%) using vapour-phase heterocatalytic cyclisation of carbonyl compounds with ammonia on a cadmium-calcium phosphate catalyst (CCP).^{111, 117–120} These pyridines are then subjected to dehydro-

cyclisation on oxide catalysts into all kinds of isomeric azafluorenes **1–4** and their alkyl-substituted in pyridine ring homologues.



R = H, Me.

Thus, comparison of the known methods used to synthesise azafluorenes reveals that the most effective (particularly, for preparing 1- and 3-azafluorenes) is the two-stage procedure based on the synthesis of phenylpyridines by Chichibabin's reaction and their subsequent dehydrocyclisation. The low yields of azafluorenes (20%–40%) at the stage of dehydrocyclisation are compensated for by the high selectivity of the process, and recycling of unconsumed phenylpyridine allows one to obtain azafluorenes in quantitative yields.

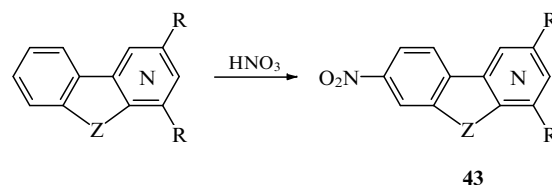
V. Transformations of azafluorenes

The chemical properties of azafluorenes and their derivatives are determined by the following factors: (1) the presence of two conjugated, fused cycles of different nature (benzene and pyridine) in one molecule; (2) the order of fusion of the indene and pyridine fragments; (3) the position and nature of functional groups in the case of substituted azafluorenes.

1. Reactions at the benzene nucleus

a. Electrophilic substitution

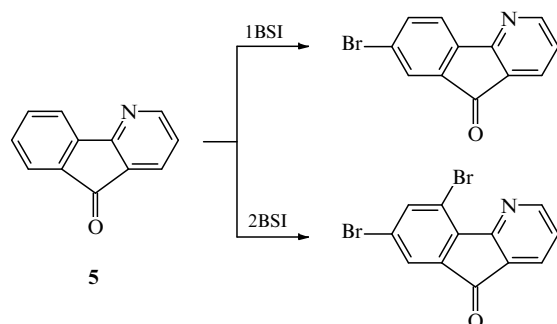
Among the reactions of electrophilic substitution, only nitration and bromination have been studied. In the nitration of unsubstituted azafluorenes,^{25, 97, 121} azafluorenes,^{6, 25, 97} and 4-azafluorenone *N*-oxide¹²² the 7-nitro derivatives **43** are always isolated as the main product irrespective of the position of the nitrogen atom in the original polycycle. These experimental results confirm the preferential orientation of electrophilic substitution inferred from quantum-chemical calculations for 1-, 3-, and 4-azafluorenes.^{5, 6}



R = H, Me; Z = CH₂, CO, CHNHA₂.

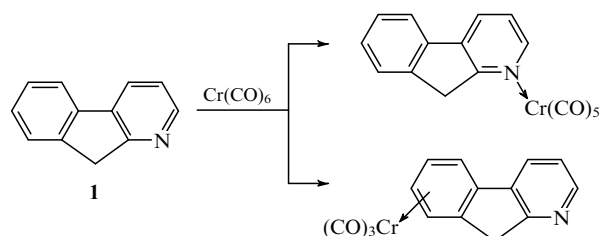
The nitro group is readily reduced (with Zn·Hg or SnCl₂ in HCl) into the amino group.⁹⁰ Carbonylation of 7-nitro-1-azafluorene in the presence of selenourea gives a mixture of 7-amino- and 7-carbamoyl-1-azafluorenes.¹²³

Bromination of 1- and 4-azafluorenes **5** and **8** in the benzene ring has been performed with bromosuccinimide (BSI) in 70% H₂SO₄ at 50 °C. This reaction gives 7-bromo-, 5,7-dibromo-, and 5,6,7-tribromo derivatives, which is in a good agreement with the calculated reactivity indices.⁵ The use of molecular bromine requires more drastic conditions: 100% H₂SO₄, 150–170 °C, autoclave.⁵



b. π -Complex formation

Nesmeyanov *et al.*^{124, 125} have studied the interaction of azafluorenes with chromium, molybdenum, and tungsten carbonyls. It has been found that only 4-azafluorene forms arenechromotricarbonyl π -complexes with the benzene ring, whereas 1-azafluorene forms mixtures of π - and n -complexes (yields 5% – 30%).



2. Reactions at the pyridine nucleus

a. Quaternisation and complex formation

The reactivity of the pyridine fragment in azafluorenes is typical of pyridine itself. Azafluorenes easily quaternise to give *N*-alkyl halides, picrates, *N*-phenacyl halides, and complexes with BF_3 .^{126–140} They also form *N*-donor complexes with copper and silver salts.¹³¹ With metal carbonyls^{124, 125} 2- and 3-azafluorenes form only n -complexes. In the case of azafluorenones, the yields of quaternary salts decrease,^{6, 126–128} apparently, due to the lower basicity of the pyridine fragment.

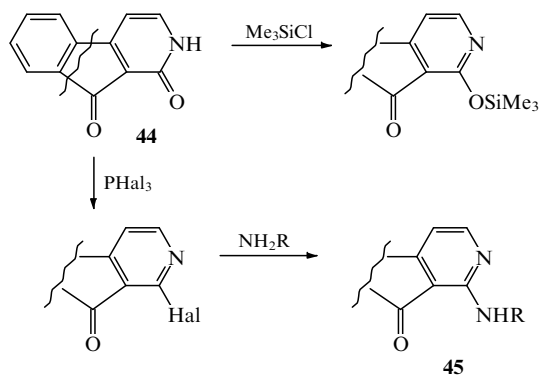
b. Deprotonation of azafluorenium salts

Quaternised azafluorenes contain in their five-membered ring the methylene group with high CH-acidity, which is readily deprotonated by basic reagents. For this reason, deprotonation of azafluorenium salts is used to obtain indenopyridine anhydrosalts containing cyclopentanpyridine fragments. The latter comprise a 10π -electron nonbenzoid aromatic system and belong to the pseudoazulene series, the isoelectronic analogues of azulene. A comprehensive review on the methods of synthesis of these azafluorene derivatives and their reactivity has been published recently.¹³²

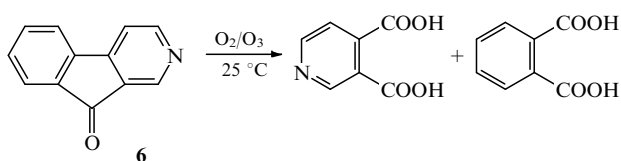
c. Oxidation

Interaction of azafluorenes and azafluorenones with hydrogen peroxide results in *N*-oxides,^{52, 109, 126, 133} which can be easily deoxygenated to free bases on heating with PBr_3 .¹²²

Oxidation of quaternary indenopyridinium salts with air or potassium ferricyanide in alkaline media gives indenopyridones.^{134, 135} The oxogroup in the α -pyridone fragment of the azafluorenediones **44** is converted into the ether group under the action of trialkylchlorosilanes and can be substituted for the halogen.⁹³ The latter is substituted for amino groups with amines under pressure.⁴⁵ The amino derivatives **45** can also be obtained from carbamoylafluorenes by Hoffmann rearrangement.

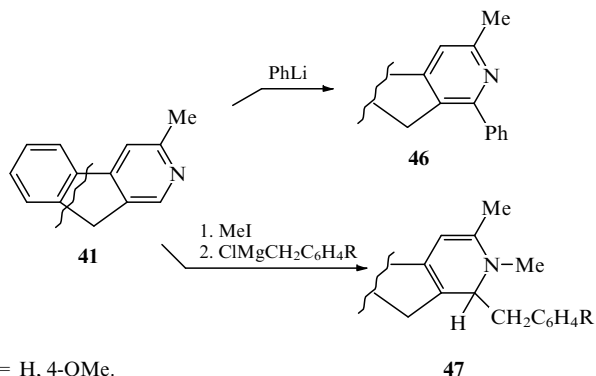


Deep oxidation of the 2-azafluorenone **6** by ozonolysis with subsequent treatment with hydrogen peroxide results in the oxidative cleavage of the tricyclic azine with the formation of cinchomeric and phthalic acids.³



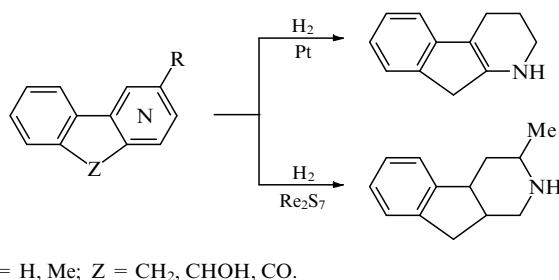
d. Arylation and benzylation

Arylation of the 2-azafluorene **41** with phenyllithium¹⁰⁹ gives its 1-phenyl derivative **46** in low yield. The efficiency of nucleophilic substitution increases when the azafluorene *N*-oxide is used. Benzylation of the azafluorene *N*-oxide or methiodide with benzylmagnesium halides also occurs at the free α -position of the pyridine ring.^{109, 136}



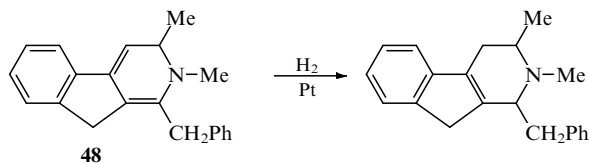
e. Hydrogenation

Catalytic hydrogenation of azafluorenes with platinum,¹¹⁰ nickel, and rhenium heptasulfide¹³⁷ is carried out at high pressure and is accompanied by partial or complete reduction of the pyridine ring.



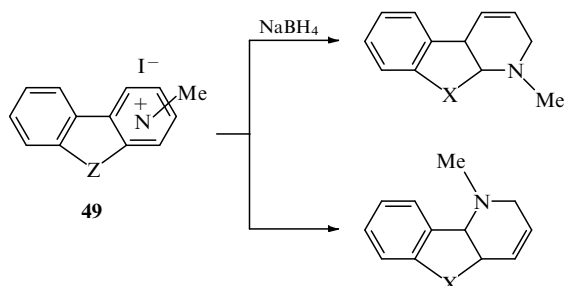
R = H, Me; Z = CH_2 , CHOH , CO .

In the case of rhenium heptasulfide, *N*-alkylation may occur if the hydrogenation is performed in an alcohol. The dihydro derivatives of 2-azafluorene **48** are reduced on platinum, nickel, or palladium into tetra- and hexahydro derivatives at atmospheric pressure.^{98–100, 136}



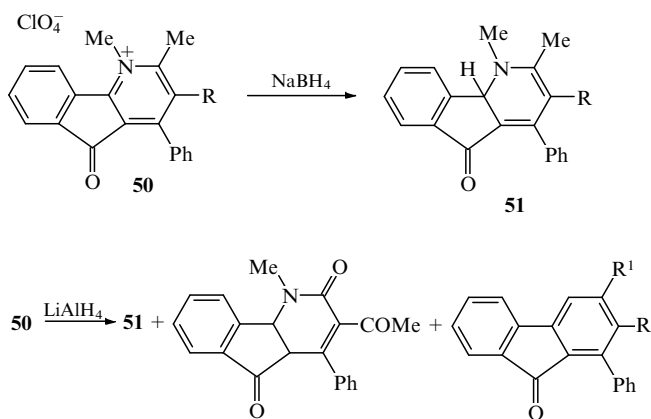
2-Azafluorenes are reduced with sodium in ethanol to indanopiperidines.^{110, 138} The stereochemistry of these hexahydro derivatives has been studied by ¹H NMR.^{138–140}

The azafluorene methiodides **49** are smoothly reduced with sodium borohydride to tetrahydro derivatives.^{6, 141–143} The residual double bond is usually localised in the β,γ-position relative to the nitrogen atom irrespective of the mode of fusion of the pyridine fragment with the cyclopentadiene ring.



Z = CO, CH₂; X = CH₂, CHOH.

Reduction of the 4-azafluorenonium perchlorate (**50**) with sodium borohydride gives 4,4a-dihydroxy derivatives (**51**). However, when lithium aluminium hydride is used, products of nucleophilic recyclisation of the pyridine ring are formed along with the derivative **51**.¹⁴³

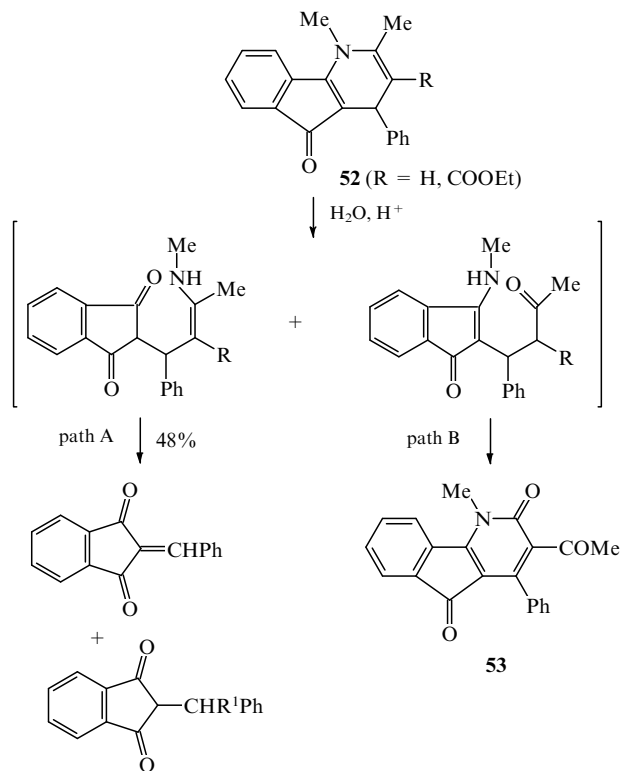


R = COOEt; R¹ = OH, NHMe.

Reduction of azafluorenium cations with sodium hydrosulfite results in indanopiperidine.¹⁴²

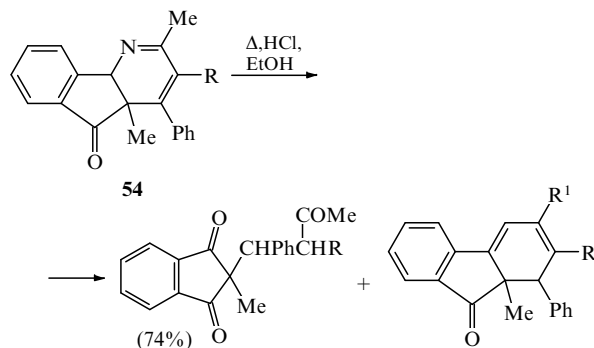
f. Hydrolysis of 1,4-dihydro-4-azafluorenes

These compounds are decyclised upon acid hydrolysis with the cleavage of the N–C bond in two directions followed by elimination of the amine fragment (route A) or recyclisation into indenopyridones **53** (route B).^{81, 144–150}



R¹ = H (27% yield), CHR¹COMe (18% yield).

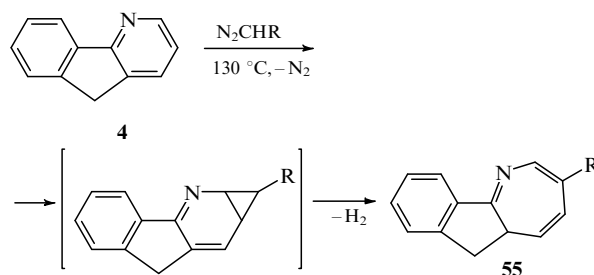
The cleavage of the N–C(4a) bond occurs more easily. Similar hydrolysis of 1,9a-dihydro-4-azafluorenone **54** gives 1,9a-dihydrofluorenone and substituted indanedione.^{81, 114, 146}



R = CO₂Et; R¹ = OH (10% yield), NH₂ (12% yield).

g. Other reactions

The thermal reaction of 4-azafluorene with ethyl diazoacetate results in indenoazepine (**55**).¹⁵¹ Apparently, the initial addition of the carbene to the double bond of the pyridine ring is followed by its expansion and dehydrogenation.¹⁵²



R = COOEt.

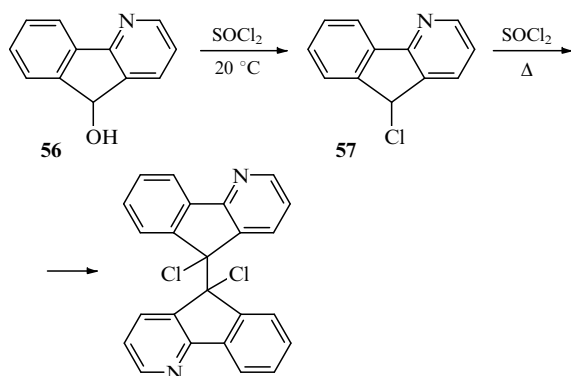
3. Syntheses involving the methylene group

a. Oxidation

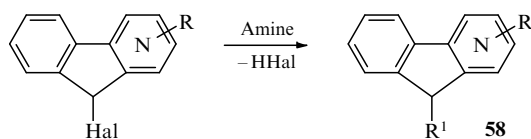
The azafluorenes **1–4** are readily oxidised to the azafluorene-9-ones **5–8** with KMnO_4 or $\text{Na}_2\text{Cr}_2\text{O}_7$ in CH_3COOH (yields 40%–60%).^{112, 116, 153} The oxidation with oxygen in the presence of the Rodionov catalyst¹⁵⁴ or an alkali in DMSO¹¹⁷ increases the yield of ketone up to 80%–90%. An exceptional tendency of 3-azafluorene to oxidation (unlike that of its isomers) has been exemplified by its quantitative conversion into a stable 9-oxo derivative by mere bubbling of air through its hexane solution.⁶ Methyl- and styryl-substituted azafluorenes are oxidised to azafluorene-9-one carboxylic acids with KMnO_4 or SeO_2 .^{108, 155} The thermal (180–220 °C) decarboxylation of these acids has been studied.^{50, 51, 64, 84}

b. Halogenation

Hydrogen atoms and the hydroxyl group at C(9) of azafluorene (**56**) are readily substituted for halogen on treatment with BSI, carbon tetrachloride (in aqueous alkali in the presence of triethylbenzylammonium salt), thionyl chloride, and hydrogen halide.^{89, 153, 156–160} It is remarkable that under halogenation conditions, 9-chloro azafluorenes (**57**) dimerise on heating.¹⁵⁶



9,9-Diiodo-1-azafluorene is formed as the sole product on attempted carbonylation of 1-azafluorene-9-ol in the presence of hydrogen iodide and rhodium iodide.¹²³ Halogen derivatives are readily reduced with zinc in ethanol¹⁶¹ and halogen atoms are smoothly substituted by nucleophiles. Thus, the interaction of 9-bromo-4-azafluorene with NH_3 and amines gives the corresponding 9-aminoazafluorenes **58**.^{157, 162} Some of them are promising as inhibitors of lipid peroxidation.

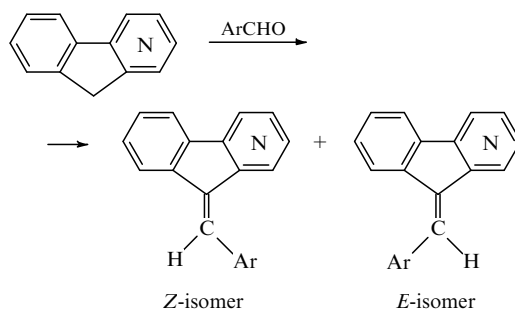


Hal = Cl, Br; R = H, Me;

$\text{R}^1 = \text{NH}_2$, N -methylpiperazine, N -benzylpiperazine, $\text{N}(\text{CH}_2\text{CH}_2\text{R}^2)_2$, where $\text{R}^2 = \text{OH}$, OCOEt , OCONH_2 .

c. Condensation with aldehydes and ketones

Aromatic and heteroaromatic aldehydes easily couple with azafluorenes at the methylene group in the presence of bases to give 9-arylidene derivatives.^{117, 153, 163–170} In some cases, the geometric isomers of these benzopyridofulvenes could be separated chromatographically which made it possible to establish their molecular structure (using X-ray structural analysis) and to relate their physical and spectral characteristics with their (*Z*)- or (*E*)-form.^{8, 17, 18, 168}

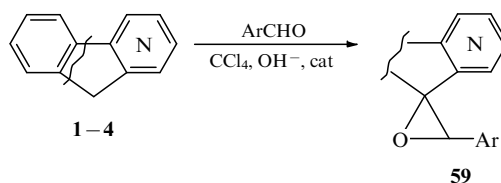


Ar = Ph, $\text{C}_6\text{H}_4\text{R}$ (where R = Br, Cl, OMe, OH, NO_2 , NMe_2),

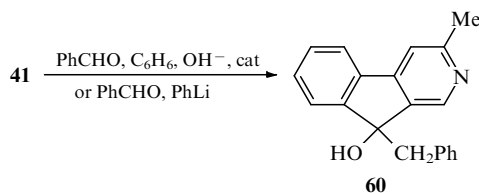
2-, 3- and 4-Py, 3-Py·MeI.

The influence of the position of the nitrogen atom in the pyridine fragment and the structure of the aromatic aldehyde on the ratio of (*Z*)- and (*E*)-isomers of 9-arylideneazafluorenes has been investigated. A possibility has been established of intramolecular through-space interaction (of the charge-transfer complex type) between the arylidene fragment and the unshared electron pair of the nitrogen atom, which can occur only in the case of 1-azafluorene derivatives.^{8, 168} 9-Alkylideneazafluorene derivatives have been prepared.¹⁶⁷ Ketones (e.g. benzophenone) also interact with azafluorenes.¹⁶³ If these condensations are carried out in the presence of air, considerable amounts of azafluorenes and 1,2-di(azafluorenylidene)ethanes are formed.^{161, 166} The methyl groups at the α - and γ -positions of the pyridine ring of azafluorene are also active as regards condensation with aromatic aldehydes, which allows synthesis of compounds of the stilbene type.^{108, 155, 163} In some cases, arylazafluorenyl ethyl alcohols¹⁶⁶ and cyclisation products of α -styryl derivatives, 3-azafluoranthenes were isolated.¹¹⁴ A series of carbocyanine dyes have been synthesised with involvement of the 3-methyl group of 2-azafluorene.¹⁶⁹

Under conditions of phase-transfer catalysis, the azafluorenes **1–4** couple with aromatic aldehydes (NaOH , CCl_4) with the formation of (*Z*)- and (*E*)-isomeric spiro(azafluorene-9,2'-oxiranes) **59**.¹⁶¹



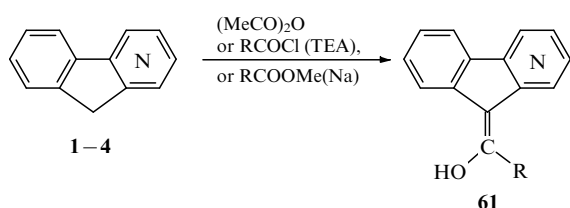
The side products of this reaction are 9,9-dichloro- and 9-benzylideneazafluorenes as well as bi(azafluorenylidene)s-9). The latter are easily formed in the alkaline dehalogenation of 9,9-dihalogenoazafluorenes.^{146, 153} The use of benzene as the organic phase results in phenyl(azafluorenyl-9)methanol (**60**), which can be also obtained by the reaction of benzaldehyde with azafluorene in the presence of phenyllithium.¹⁷⁰



d. Acylation and alkylation

The azafluorenes **1–4**, like fluorene, are acylated at C(9) with acetic anhydride,¹⁷¹ acyl chlorides,^{130, 183} and alkylcarboxylic acid esters in the presence of alkali metals.^{170, 172} However, unlike 9-acylfluorenes, acyl derivatives of azafluorenes occur as enols

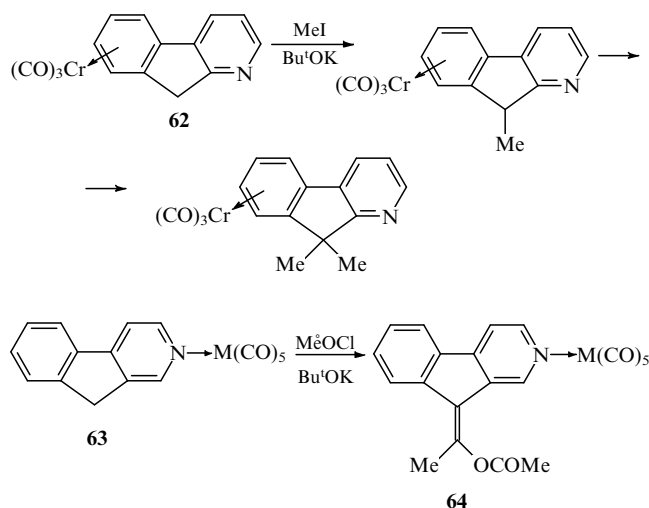
61, which seems to be assignable to the higher CH-acidity of azafluorenes.



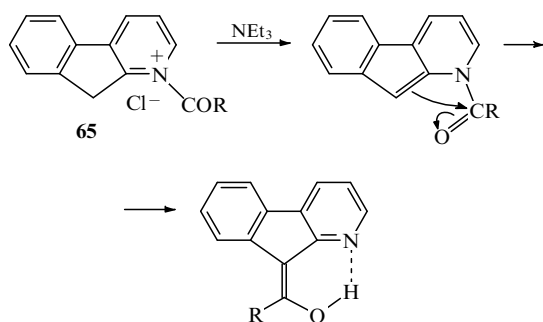
R = Me, Et, Ph, , PhCH=CH, PhOCH₂.

Spectroscopic studies have shown that in the crystalline state as well as in polar and aprotic solvents 9-formyl-4-azafluorene exists in the enolic form, whereas in nonpolar and protic solvents, it is a mixture of aldehyde and enolic forms.¹⁷³

Reactions of alkyl halides and acid chlorides with arenochrometricarbonylazafluorenes under deprotonation conditions have been studied.^{124, 125} It has been shown that π -complexes **62** are alkylated at C(9) and N-donor complexes **63** are acylated analogously, with the formation of enol acetates **64**.



Treatment of 1-acyl-1-azafluorenium chlorides (**65**) with bases in benzene is accompanied by the formation of unstable, deep-coloured 1-acyl-1*H*-indenopyridines. Under the action of BF₃ they undergo a 1 $\rightarrow$ 3 acyl shift and are quantitatively converted into 9-acylindenopyridines, which exist in the enolic form stabilised by an intramolecular hydrogen bond.¹³⁰ No acyl shift occurs in the case of isomeric azafluorenes.

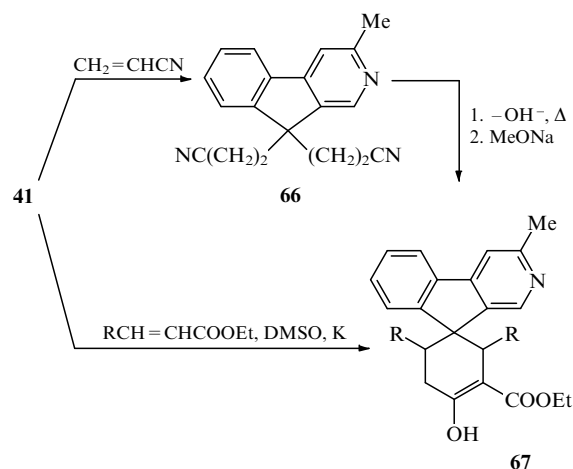


R = Me, Ph, C₆H₄NO₂-4.

Aralkylation of 4-azafluorene has been carried out at C(9) using a mixture of veratryl alcohol and veratraldehyde in the presence of KOH.¹⁶⁵

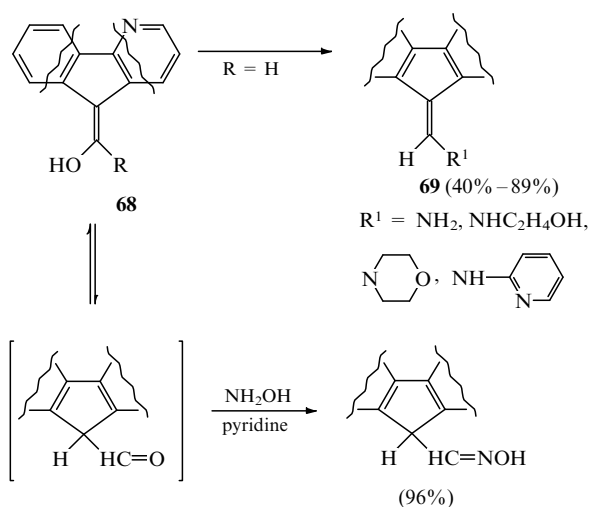
2- And 4-azafluorenes are readily alkylated under conditions of the Michael reaction²¹ and are cyanoethylated with acrylonitrile in the presence of the Rodionov catalyst.^{114, 154, 174, 175} The

9,9-bis(cyanoethyl)azafluorenes (**66**) obtained are then hydrolysed to dibasic acids thus which give after esterification entered into the Dieckmann condensation to spiro(azafluorene-9,1'-cyclohex-3-enes) (**67**). Analogous spiro-compounds are formed in one step with 20%–54% yields when esters of α,β -unsaturated acids react with azafluorene in the presence of potassium.¹⁷⁶

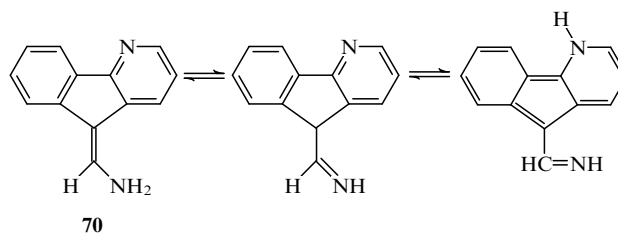


e. Reactions of 9-methylene derivatives of azafluorenes

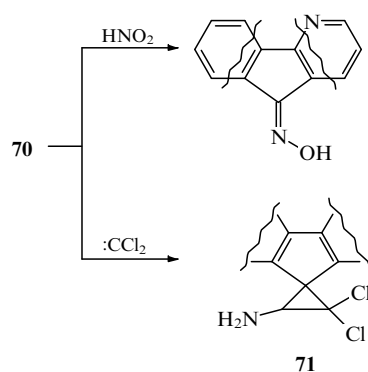
9-Hydroxymethyleneazafluorenes (**68**) are converted by nucleophiles (ammonia or amines) into 9-aminomethylene derivatives (**69**), whereas with hydroxylamine, they form a stable 9-formyl-azafluorene oxime.¹⁷²



9-Aminomethylene-4-azafluorene **70** exists as enamine and two tautomeric imines. Quantum-chemical calculations as well as UV and IR spectral data indicate that this compound has the enamine structure.¹⁷⁷

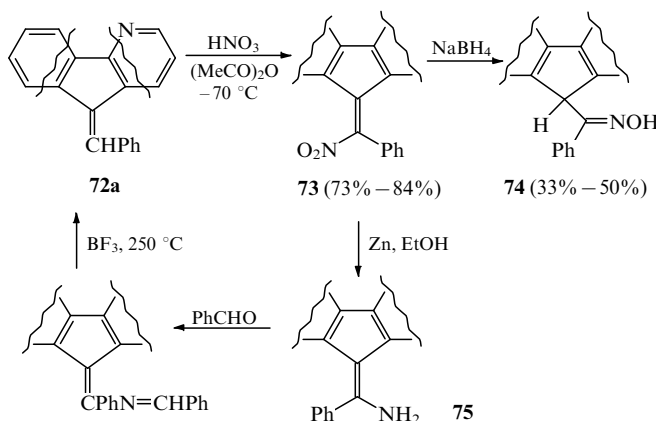


Its nitrosation gives the 2-azafluorenone oxime. Dichlorocarbene adds to the exocyclic C=C bond of the compound **70** to give the spirocyclopropane derivative **71**.

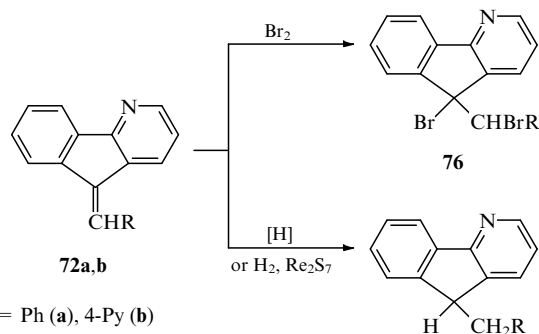


Acylation of the enamine **70** gives normal mono- or diacetyl derivatives.

Nitration of benzyldeneazafluorene (**72a**) with acetyl nitrate results in the substitution of hydrogen at C(10) with the formation of 9- α -nitrobenzyldeneazafluorenes (**73**) as (*Z*)- and (*E*)-isomers in a ratio of 1 : 2.5; these compounds can be reduced the oxime **74** or amine **75**.¹⁷² Condensation of the latter with aldehydes smoothly gives Schiff's bases with the *S-trans*-configuration of the azadiene fragment.¹⁷⁸ Thermolysis of these imines in the presence of BF_3 gives the original compound, **72a**.

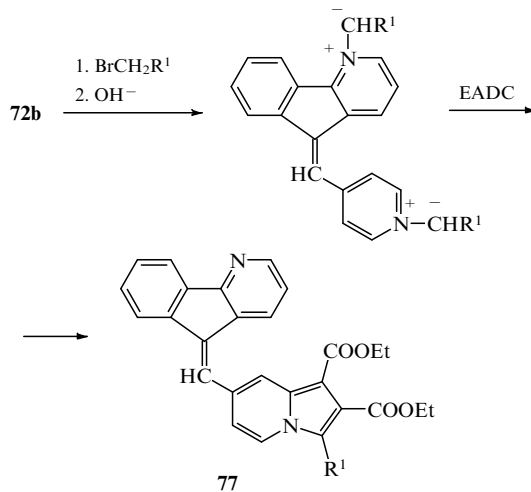


The exocyclic double bond of benzopyridofulvenes of the **72a,b** type is readily reduced with lithium aluminium hydride¹⁶³ or a mixture of benzyl alcohol with KOH at 200 °C.¹⁶⁵ In the case of pyridylmethylenazafluorene, catalytic hydrogenation over Re_2S_7 also occurred at this bond and did not affect the pyridine rings.¹⁷⁹



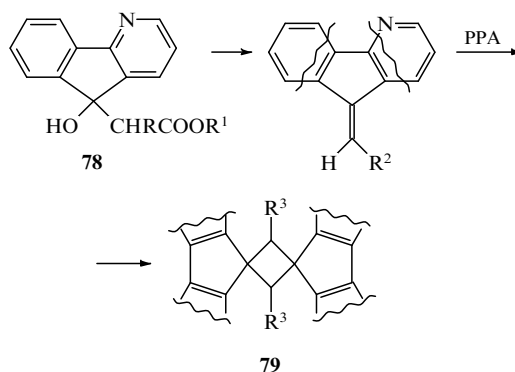
The latter finding suggests that the substrate is coordinated at the acidic centres of rhenium heptasulfide through the π -excessive fulvene fragment rather than through the pair of unshared electrons of the nitrogen atom. Calculations on this type of fulvene system provide support for the localisation of the negative charge at the carbon atoms of the exocyclic double bond.^{8,17} The bromine molecule readily adds at this double bond in the compounds **72a,b** to give dibromo derivatives **76**.

The pyridylmethylenazafluorene **72b** forms a double salt with bromoacetophenone, which generates a double ylide under the action of bases. This ylide adds only one molecule of ethyl-acetylenedicarboxylic acid (EADC) and only at the pyridyl radical to form the adduct **77**; the phenacyl substituent at N_4 of the azafluorene skeleton is split off in the process.¹⁷



The Wagner hydroxylation of the exocyclic $\text{C}=\text{C}$ bond results in the glycol.^{180, 181}

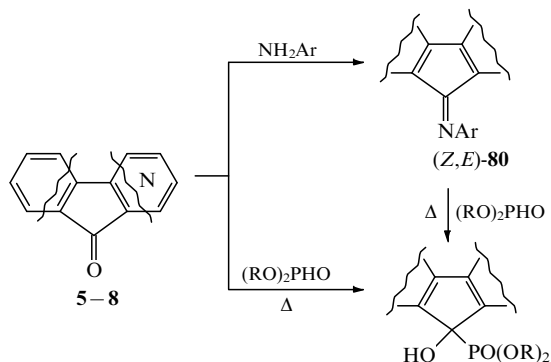
2-(9-Hydroxyazafluoren-9-yl)propionic and (9-hydroxyazafluoren-9-yl)acetic acids or their esters **78** were converted via 9-methylene derivatives into dispirobis(4-azafluorene)-9-1',3'-cyclobutanes **79**.^{161, 182}



4. Syntheses involving the carbonyl group of azafluoren-9-ones

a. Condensation with amines and CH-active compounds

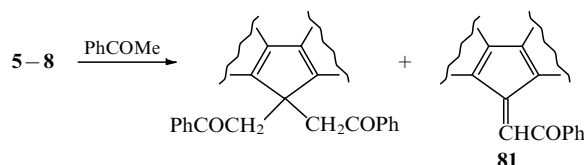
The azafluorenones **5–8** give oximes, hydrazones, semicarbazones,^{2, 6, 45, 183} and Schiff's bases **80**.^{116, 184}



Higher yields of the latter compounds have been achieved with the use of BF_3 as the catalyst. The dependence of the ratio of the configurational *Z,E*-isomers of the ketimines **80** on the nature of the amine component used for condensation was studied by ^1H NMR. An alternative synthesis of arylazomethines of the type **80** has been carried out by condensation of azafluorenes with *p*-nitrosoanilines followed by reduction of the intermediate nitrones with zinc in ethanol.^{158, 184}

The Schiff's bases **80**, like the original azafluorenes, add dialkyl phosphites to give the corresponding 9-azafluorenyl-phosphonates.¹⁸⁵ 9-Iminoazafluorenes were converted into 9-amino derivatives with Zn(Fe) in AcOH or Ac_2O ,^{19, 45} NH_2-NH_2 (Raney Ni)¹⁸³ or LiAlH_4 .¹⁸⁴

Under alkaline conditions, azafluorenes condense with acetophenone to give 9,9-bis(phenacyl)- and 9-phenacylidene derivatives **81**.^{180, 181}



b. Reduction

Heating of azafluorenes with hydrazine hydrate in an autoclave results in the reduction of the oxo-group to the methylene group in high yield.^{3, 92, 186} In lower yields azafluorenes are formed on reduction with zinc amalgam in hydrochloric acid.³ Sodium borohydride reduces azafluorenes only to alcohols¹⁴²⁻¹⁴⁴ which are smoothly esterified with acid anhydrides¹⁸⁷ and acid chlorides.¹⁴¹

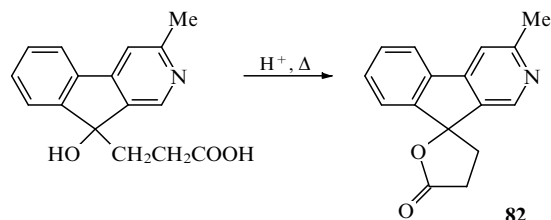
c. Interaction with organometallic compounds

Azafluorenes react with phenyl- and methyl lithium and with benzylmagnesium chloride to give the ordinary products of nucleophilic addition, i.e., the corresponding tertiary alcohols.¹⁸⁷ The yield of alcohols depends on the position of the nitrogen atom and the presence of substituents.^{141, 142} These alcohols are easily dehydrated in acid media or in the presence of P_2O_5 .^{165, 167, 187} In the presence of zinc, the esters of α -bromocarboxylic acids add to the $\text{C}=\text{O}$ group of azafluoren-9-ones to give the corresponding 9-substituted azafluoren-9-ols.¹⁶¹

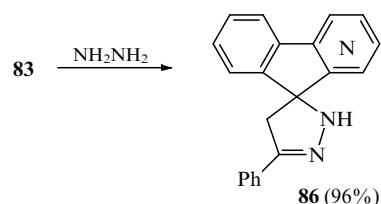
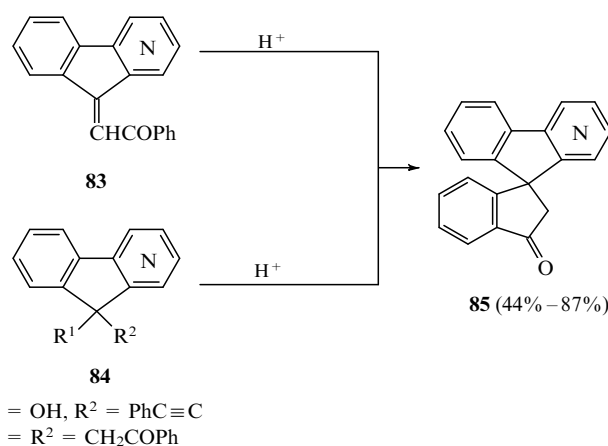
5. Cyclisation reactions involving substituents

a. Synthesis of spiro-coupled derivatives

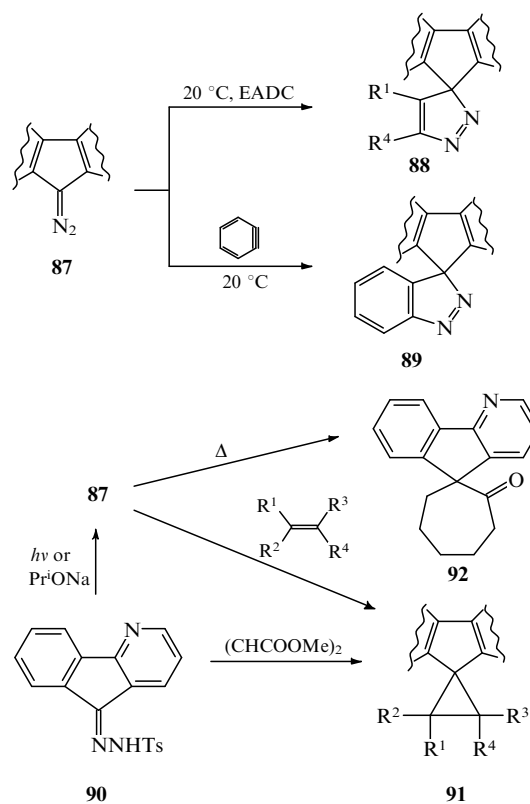
Heating of β -(9-hydroxy-2-azafluoren-9-yl)propionic acid in acid media results in cyclisation to the spiro lactone **82**.¹⁵⁴



9-Phenacylideneazafluorenes **83** and 9-hydroxy-9-phenylethynylazafluorenes **84** also enter into acid-catalysed cyclocondensation to give spiro compounds of the type **85** with indanone fragments.^{180, 181} Condensation of the phenacylidene derivative **83** with hydrazine gives a spiro-fused pyrazoline **86** in quantitative yield.¹⁸⁰



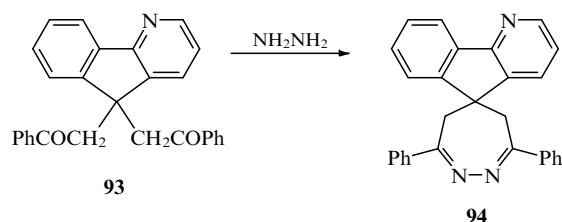
9-Diazo-4-azafluorene (**87**) gives spiro(4-azafluorene-9,3'-3*H*-pyrazole) (**88**),¹⁸⁸ the product of cycloaddition of EADC, and an analogous spiro-compound **89** with dehydroxybenzene.¹⁸⁹ Dimethyl fumarate reacts with tosylhydrazide **90** on boiling in benzene in the presence of sodium alkoxide to give spiro(4-azafluorene-9,3'-cyclopropane) (**91**).¹⁸⁸



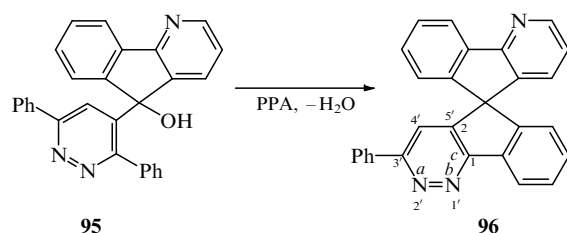
$\text{R}^1 = \text{COOMe}, \text{Ph}, \text{CHO}, \text{SiMe}_3, \text{CN};$
 $\text{R}^2, \text{R}^3 = \text{H}; \text{R}^4 = \text{COOMe}.$

Similar compounds were obtained upon interaction of the derivative **87** with certain unsaturated compounds.¹⁹⁰ In the case of cyclohexanone, spiro(4-azafluorene-9,2'-cycloheptanone) (**92**) was isolated.

Treatment of the diketone **93** with hydrazine results in spiro(4-azafluorene-9,5'-diazepine) **94**.¹⁹¹

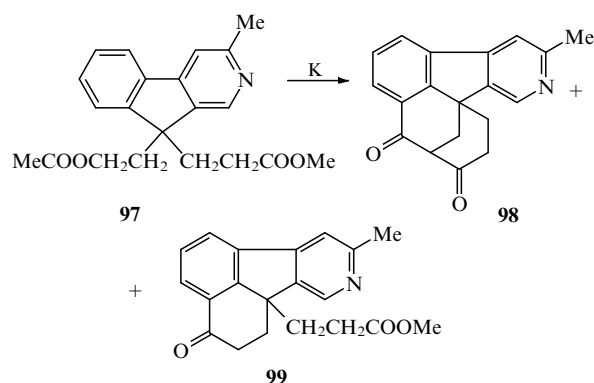


Intramolecular cyclodehydration of 9-(pyridazin-4-yl)azafluorenol (**95**) gives spiro{4-azafluorene-9,5'-indeno[1,2-*c*]-pyridazine} (**96**).¹⁹¹

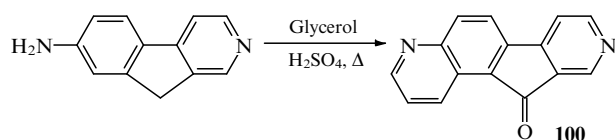


b. Annellation of the benzene ring

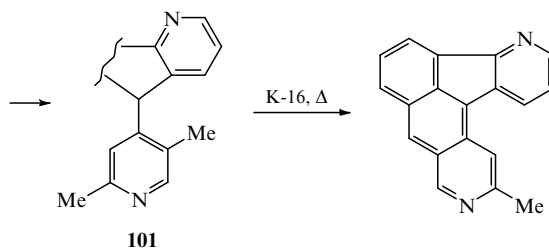
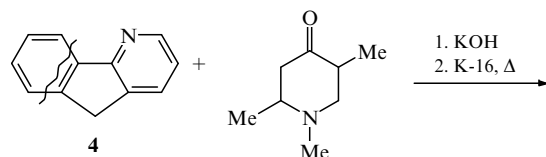
In the presence of potassium the diester of a dibasic acid of the azafluorene series **97** gives two cyclocondensation products, viz., **98** and **99**.¹⁶²



Only one cyclisation product **100** has been obtained in low yield from 7-amino-2-azafluorene by the Skraup reaction.¹⁶⁴

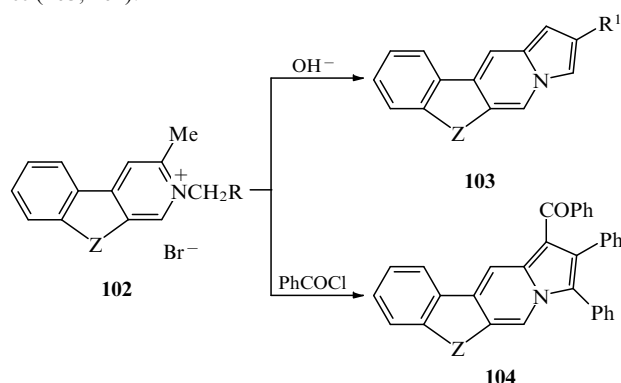


4-Azafluorene condenses with 1,2,5-trimethyl-4-piperidone in the presence of KOH to give an unstable product, which was dehydrogenated without isolation into 9-pyridyl-4-azafluorene **101**.¹⁵⁷ The latter was converted into pyridoazafluoranthene by catalytic dehydrocyclisation.



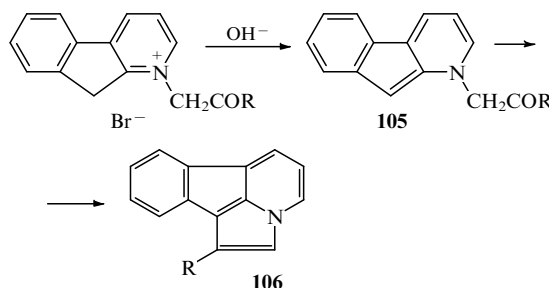
c. Annellation of the pyridine ring

3-Methyl-*N*-phenacyl-2-azafluorenium bromides (**102**) cyclise under condition of the Chichibabin reaction into indenoindolizines (**103**, **104**).^{127, 128}



$\text{R} = \text{COMe}, \text{COPh}$; $\text{R}^1 = \text{Me}, \text{Ph}$; $\text{Z} = \text{CH}_2, \text{CO}, \text{C}(\text{OH})\text{Ph}$.

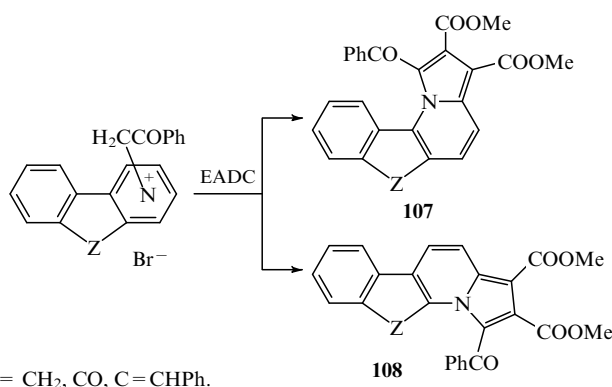
However, in the case of the 1-azafluorenium this reaction does not take place, and stable anhydro bases **105** are formed instead.^{121, 130}



$\text{R} = \text{Ph}, \text{C}_6\text{H}_4\text{NO}_2-4$.

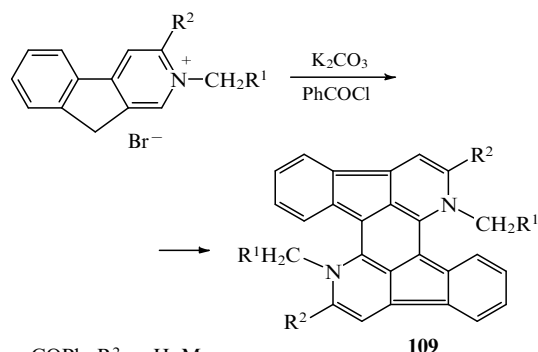
Nevertheless, the latter were successfully converted into indenoindolizines **106** by thermolysis *in vacuo*.

Isomer-*N*-phenacyl azafluorenium bromides enter into 1,3-dipolar cycloaddition reactions with EADC to give indenoindolizines **107** and **108** with different fusion of the rings.^{6, 127, 128}



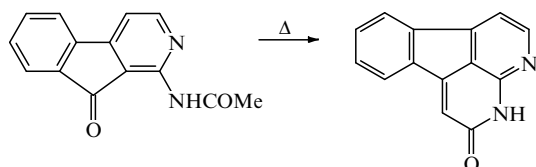
$\text{Z} = \text{CH}_2, \text{CO}, \text{C}=\text{CHPh}$.

The quaternary salts of 2- and 4-azafluorenium are deprotonated in the presence of benzoyl chloride to give dimers (in low yields) in the form of *NH*-diazafuoranthenes **109**.¹²⁸

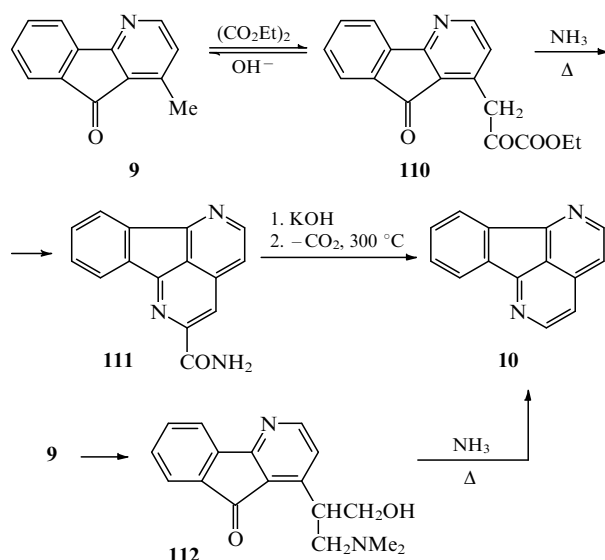


$R^1 = \text{COPh}$; $R^2 = \text{H, Me}$.

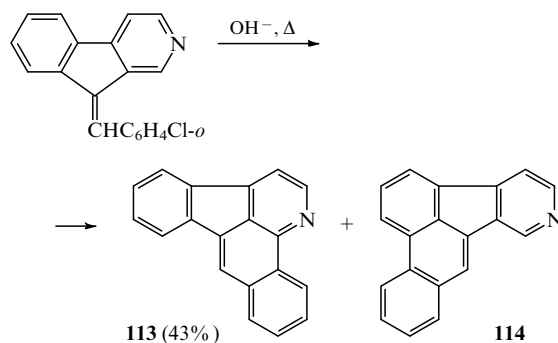
1-Acetylamino-2-azafluorenone was converted into 3*H*-3,4-diazafuoranthene-2-one on heating in DMF in the presence of potassium alkoxide.⁴⁵



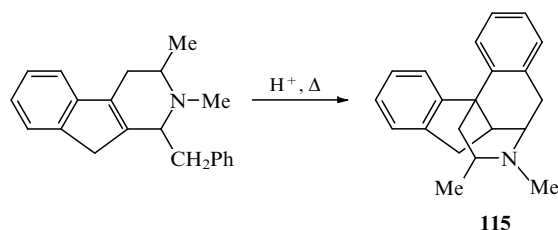
Condensation of diethyl oxalate with the alkaloid onychin (**9**) gives ethyl(9-oxo-4-azafluorenyl)pyruvate (**110**).⁴⁵ Its heating with ammonia results in 1,6-diazafuoranthene-2-carboxamide (**111**). The latter was converted by a two-step procedure into the alkaloid eupolauridine (**10**); it could also be obtained by an independent synthesis from the compound **112**, the product of condensation of onychin (**9**) with formaldehyde and dimethylamine.



Polycyclic heterocycles **113** and **114** were obtained on heating of 9-(2-chlorobenzylidene)-2-azafluorene in the presence of alkali.¹⁶⁴



Cyclisation of 1-benzyl-1,2,3,4-tetrahydro-2-azafluorene in orthophosphoric acid resulted in a structural analogue of morphine **115** in a low yield.¹³⁶

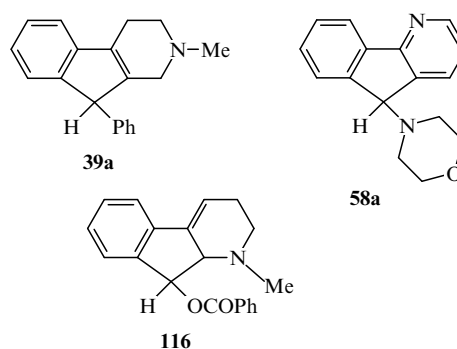


VI. Biological activity of azafluorene derivatives

Azafluorene derivatives display a broad spectrum of biological activities which gives a strong impetus to the synthesis and further biotesting new compounds of this series. 2-Methyl-9-phenyl-1,2,3,4-tetrahydroxy-2-azafluorene (**39a**) has been introduced into clinical practice as an antiallergic drug.^{100, 192} Some of its analogues manifest potent spasmolytic, adrenolytic, anaesthetic, and antihistamine activity.^{2, 193}

Dihydro- and hexahydro-derivatives of 2-alkylaminoalkyl-9-phenyl-2-azafluorene possess antiarrhythmic and bactericidal activities.¹⁰¹

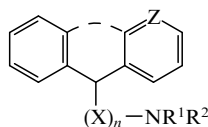
4-Azafluorene-*N*-oxide inhibits the effects of adrenaline and secretion of gastric juice.¹³³ 1,4-Dihydro-derivatives and 9-amino-derivatives of 4-azafluorene **58a** exhibit a vasodilator activity and manifest the properties of peroxidation inhibitors.^{194–196}



As follows from the review of antiviral preparations,¹⁹⁷ alkyl-, carboxy-, and cyano-derivatives of 1-azafluorene have been recommended as antiinfluenza drugs. Derivatives of 1,2,4,9a-tetrahydro-1-azafluorene-3-carboxylic acid are considered as simple analogues of ergot alkaloids.^{73, 74, 198, 199} 1-Azafluorene and its 9-hydroxy-derivative methiodides display a broad spectrum of antibacterial activities.¹²⁶ Several tetrahydro-2-azafluorenes **116**¹⁴¹ and 9-substituted 1-azafluorenes (semicarbazones, tosylhydrazones, and arylidene-derivatives) are characterised by neurotropic activity and low toxicity.²⁰⁰ The results of antitumour assay of certain azafluorenones have been documented.^{201, 202}

Azafluorene derivatives exhibit a pesticide activity and regulate plant growth and development.^{17, 203, 204} An extensive body of evidence concerning the diverse biological activities of these compounds has also been accumulated in the patent literature over the recent years; these data are not considered in the present review.

It should be emphasised that 9-substituted azafluorenes incorporate a fragment of a potentially pharmacophore ('magic') group **117**, which is present in the molecules of numerous drugs affecting biological systems via cholinergic, adrenergic, and histamine receptors.²⁰²



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It may therefore be expected that a search among these azafluorene derivatives for compounds endowed with a high biological activity is a very promising approach.

In conclusion, the authors express the hope that the review presented will provide further impetus to the expansion and intensification of studies into the chemistry of azafluorenes and will generate professional interest among scientists in related fields (pharmacologists, biochemists, etc.) in this group of heterocyclic compounds, which has currently become chemically available.

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2,3-Dihydrofurans in the synthesis of heterocyclic compounds

M-G A Shvekhgeimer

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Abstract. Published data on the synthesis of heterocyclic compounds based on 2,3-dihydrofuran and its derivatives are surveyed, described systematically, and analysed for the first time. The bibliography includes 206 references.

I. Introduction

2,3-Dihydrofuran and its derivatives are representatives of cyclic vinyl ethers (ethers of enols). They are highly reactive and readily undergo various chemical transformations. Vast information on the chemistry of 2,3-dihydrofuran and its derivatives is available; however, no review papers on this topic have been published so far. Only two monographs^{1,2} contain some data concerning the chemistry of compounds of the 2,3-dihydrofuran series including a few examples of chemical transformations of 2,3-dihydrofurans.

2,3-Dihydrofuran and its derivatives incorporate a reactive double bond and, hence, they readily enter into various addition reactions. Among them, cycloaddition and addition of azoles or azines are especially interesting. Compounds obtained in these reactions, the molecules of which incorporate tetrahydrofuryl groups and residues of pyrimidine derivatives or derivatives of other nitrogen-containing heterocyclic systems, exhibit a broad spectrum of biological activity. Some of them have been found to be effective antitumour preparations.

Since 2,3-dihydrofurans are cyclic vinyl ethers, they readily undergo recyclisation reactions and are thus converted into other cyclic systems. It is also noteworthy that hydrogen atoms in 2,3-dihydrofurans are capable of being substituted by various fragments under mild conditions.

The data surveyed in our review are classified according to the types of reaction into which 2,3-dihydrofuran and its derivatives enter. In Section II, [2 + 1]-, [2 + 2]-, [3 + 2]-, [4 + 2]- and some other cycloaddition reactions involving compounds of the 2,3-dihydrofuran series are considered successively. Section III is devoted to the transformations of 2,3-dihydrofurans according to recyclisation reaction routes. The reactions involving substitution of hydrogen atoms in the molecules of 2,3-dihydrofuran and

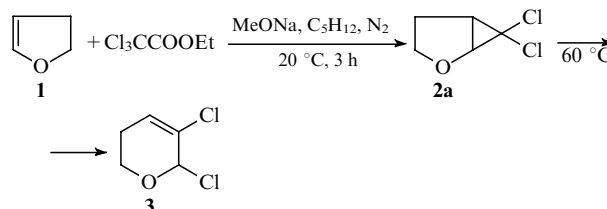
its derivatives are discussed in Section IV. Section V includes the available data on the addition of various reagents to the double bond in 2,3-dihydrofurans.

II. Cycloaddition reactions

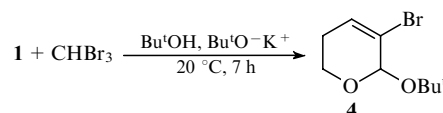
1. [2 + 1]-Cycloaddition

In the studies on the interaction of carbenes with 2,3-dihydrofuran and its derivatives two main methods are used for the generation of these highly reactive species (from gem-polyhalo-derivatives and from diazo compounds).

The reaction of 2,3-dihydrofuran **1** with ethyl trichloroacetate in the presence of sodium methoxide gives 6,6-dichloro-2-oxabicyclo[3.1.0]hexane **2a**, which is converted into 2,3-dichloro-5,6-dihydro-2*H*-pyran **3** on heating to 60 °C (yield 90%).³



The reaction of the compound **1** with bromoform, carried out in *tert*-butyl alcohol in the presence of potassium *tert*-butoxide at 20 °C, afforded, instead of the expected 6,6-dibromo-2-oxabicyclo[3.1.0]hexane, the product of its isomerisation and interaction with the solvent, namely, 3-bromo-2-*tert*-butoxy-5,6-dihydro-2*H*-pyran **4** (yield 21%).³



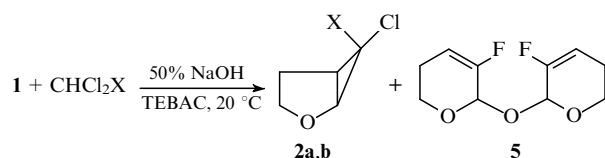
The reaction of 2,3-dihydrofuran **1** with trihalomethanes in the presence of aqueous sodium hydroxide and benzyltriethylammonium chloride (BTEAC) (the Rodionov catalyst) has also been carried out.⁴

In the case where dichlorofluoromethane was used, in addition to the cyclopropane derivative **2b**, di(3-fluoro-5,6-dihydro-2*H*-pyran-2-yl) ether **5** arising from a rearrangement product similar to **3** was isolated in 40% yield.

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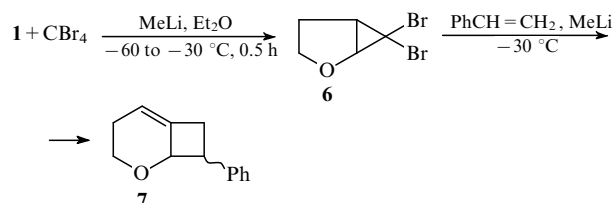


X Yield (%)

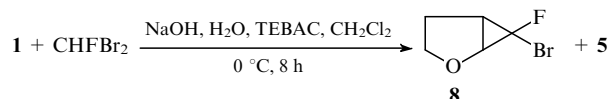
Cl 71 (**2a**)

F 30 (**2b**) + 40 (**5**)

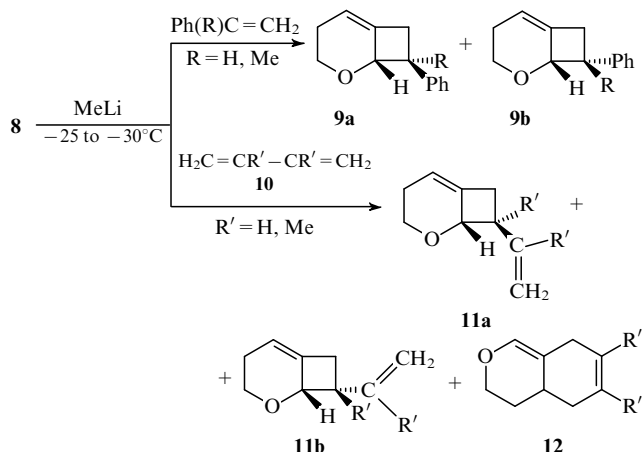
6,6-Dibromo-2-oxabicyclo[3.1.0]hexane **6**, formed upon treatment of 2,3-dihydrofuran **1** and carbon tetrabromide with methyllithium under an inert atmosphere, reacts with styrene to give a mixture of isomers of the cyclobuta[b]pyran derivative **7** (yield 24%).⁵



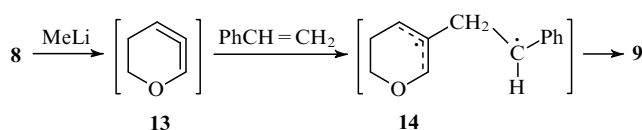
A mixture of *exo*-6-bromo-*endo*-6-fluoro-2-oxabicyclo[3.1.0]hexane **8** (yield 25%) and the ether **5** (yield 35%) was obtained by the reaction of 2,3-dihydrofuran with dibromofluoromethane in the presence of sodium hydroxide and BTEAC.⁵



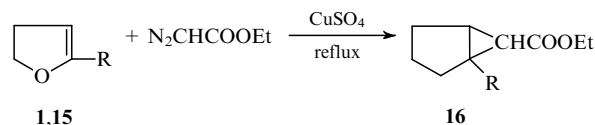
The bromofluoro-derivative **8** reacts with styrene or α -methylstyrene in the presence of methyllithium to give a mixture of *exo*- and *endo*-isomers **9a,b** (yield 54%), whereas the reaction of **8** with dienes **10** under the same conditions leads to a mixture of *exo*- and *endo*-isomers **11a,b** (yield 57%–80%) and compound **12**.⁵



Christl and Braun⁵ have proposed a scheme for the formation of the bicyclic systems **9** and **11** (using compounds **9** as an example) *via* the intermediate formation of cyclic 1,2-diene **13** and biradical **14**.

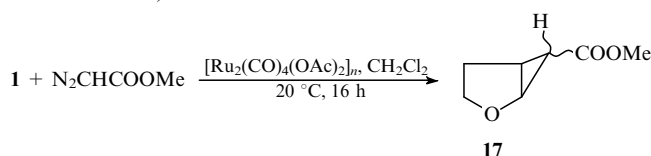


Refluxing of ethyl diazoacetate with an excess of 2,3-dihydrofuran **1** or 5-methyl-2,3-dihydrofuran **15** in the presence of copper(II) sulfate has led to 2-oxabicyclo[3.1.0]hexane derivatives **16** (yields 76% and 79%, respectively).⁶

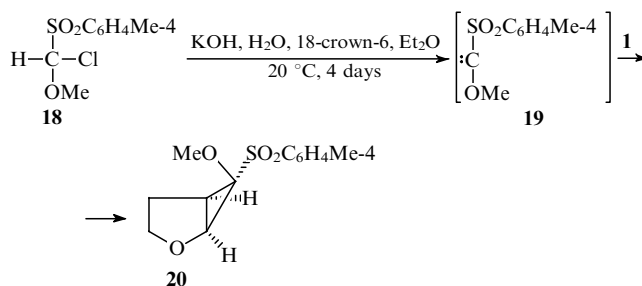


R = H, Me.

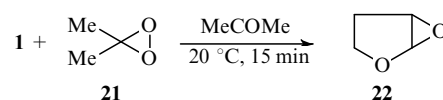
The compound **1** reacts with methyl diazoacetate in the presence of a ruthenium catalyst even at 20 °C to afford methyl 2-oxabicyclo[3.1.0]hexane-6-carboxylate **17** (yield 62%, *E*:*Z* isomer ratio 97:3).⁷



By treatment with aqueous potassium hydroxide in the presence of a crown ether, chloro(methoxy)methyl *p*-tolyl sulfone **18** has been converted into carbene **19**, which was introduced *in situ* into the reaction with 2,3-dihydrofuran **1**; *endo*-6-methoxy-*exo*-6-(tolyl-*p*-sulfonyl)-2-oxabicyclo[3.1.0]hexane **20** was thus synthesised in 48% yield.⁸

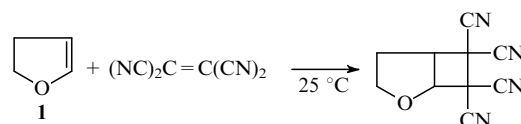


Oxidation of the enol ether **1** with dimethyldioxirane **21** at room temperature leading to 2,6-dioxabicyclo[3.1.0]hexane **22** can also be regarded formally as [2+1]-cycloaddition.⁹

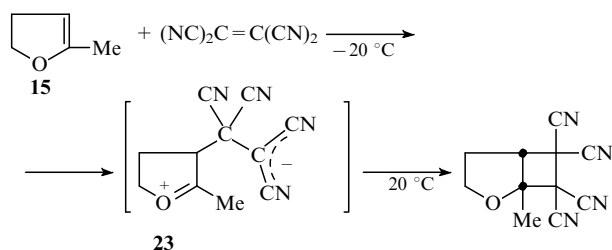


2. [2+2]-Cycloaddition

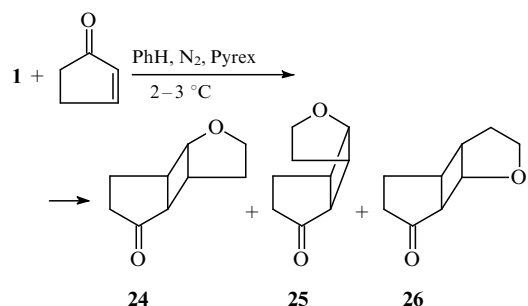
In 1973, Huisgen and Steiner¹⁰ studied the reaction of 2,3-dihydrofuran **1** with tetracyanoethene and determined its rate constant ($k_2 \times 10^3 = 22.6 \text{ litre mol}^{-1} \text{ s}^{-1}$). They suggested that this reaction involves the intermediate formation of a biradical or a zwitterion.



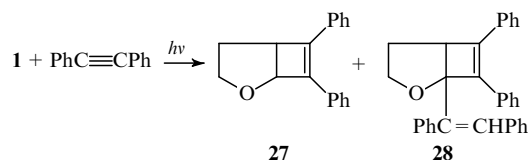
Fries and Gollinck¹¹ believe that the reaction of 5-methyl-2,3-dihydrofuran **15** with tetracyanoethene at –20 °C affords the zwitterion **23**, which is converted into the final adduct at 20 °C.



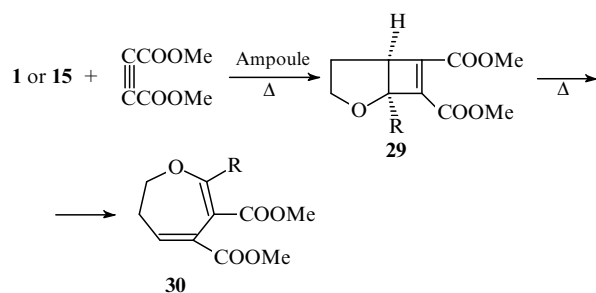
Photochemical reaction of the enol ether **1** with cyclopent-2-enone results in the formation of three products of [2+2]-cycloaddition: *exo*-**24** (head-to-tail), *endo*-**25** (head-to-tail) and *exo*-**26** (head to head), in 99% overall yield. The ratio of the isomers **24** : **25** : **26** = 75 : 3 : 22.¹²



When a mixture of the enol ether **1** and diphenylacetylene is irradiated with the light of a low-pressure mercury lamp for 3 days, two compounds are formed: 6,7-diphenyl-2-oxabicyclo[3.2.0]hept-6-ene **27** (yield 11%) and compound **28** resulting from the addition of the adduct **27** to the second diphenylacetylene molecule (yield 5%).¹³

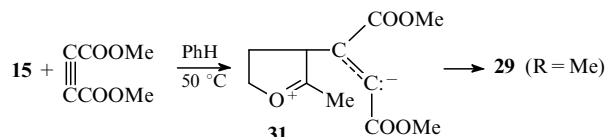


By thermal condensation of dihydrofurans **1** or **15** with dimethyl acetylenedicarboxylate, one can obtain [2+2]-cycloaddition products **29**, which are converted into 2,3-dihydrooxepine derivatives **30** on prolonged keeping at 200 °C.¹⁴

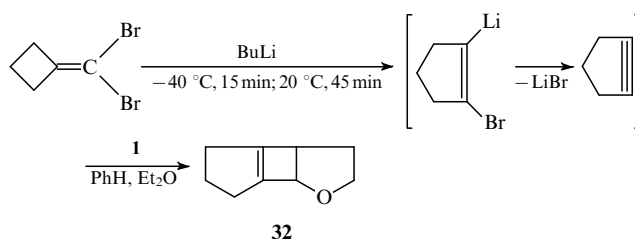


R	Catalyst	Solvent	T / °C	Time / h	Yield (%)	
					29	30
H	Pr ₂ NEt	PhMe	110	1	39	—
Me	Pr ₂ NEt	PhMe	60	1	41	—
Me	Pr ₂ NEt	DMF	60	0.5	85	—
Me	Pr ₂ NEt	DMSO	60	0.5	95	—
Me	—	PhMe	200	12	—	85

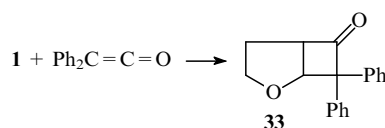
In the opinion of Fries and Gollinck,¹⁵ the reaction of enol ether **15** with dimethyl acetylenedicarboxylate is reversible and occurs *via* the formation of the intermediate bipolar ion **31**.



Treatment of dibromomethylenecyclobutane with butyllithium affords 1-lithio-2-bromocyclopentene, which eliminates lithium bromide under the reaction conditions being thus converted into cyclopentyne, which enters *in situ* into a [2+2]-cycloaddition reaction with the enol ether **1**; this leads to adduct **32** in 35% yield.¹⁶

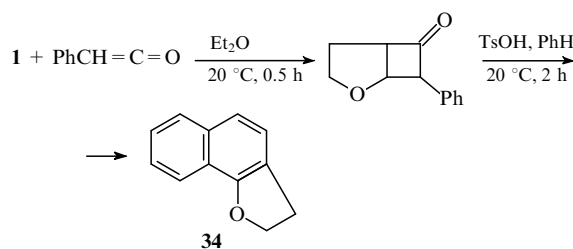


The compound **1** reacts smoothly with diphenylketene at 0 °C to give 7,7-diphenyl-2-oxabicyclo[3.2.0]heptan-6-one **33** in a quantitative yield.¹⁷

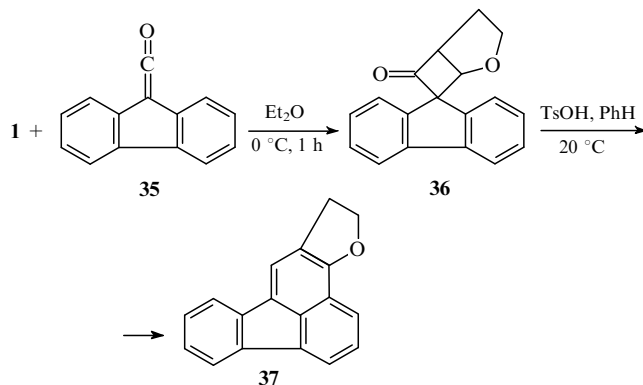


A study of the rate of [2+2]-cycloaddition of diphenylketene to various enol ethers has shown that the compound **1** reacts with the ketene 350 times faster than 2,3-dihydropyran and 20 times faster than ethyl vinyl ether.^{18, 19}

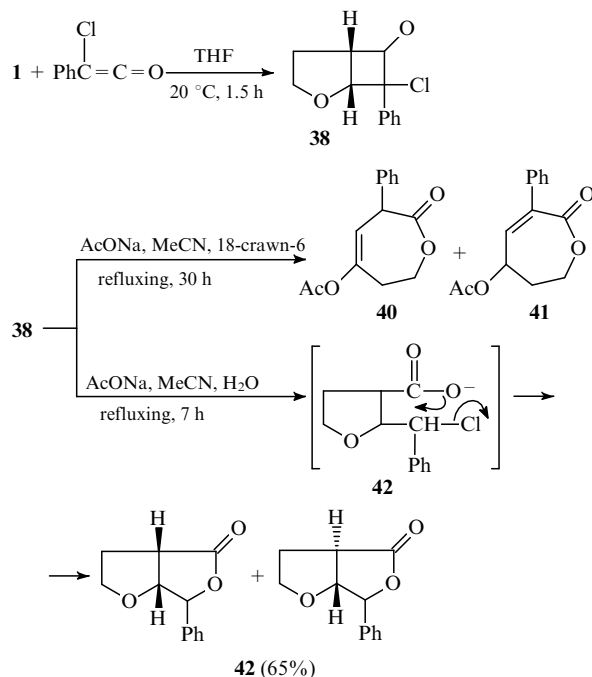
The enol ether **1** readily reacts with phenylketene to give 7-phenyl-2-oxabicyclo[3.2.0]heptan-6-one in 80% yield; the latter is converted into the naphthofuran derivative **34** (yield 30%) on treatment with toluene-*p*-sulfonic acid.²⁰



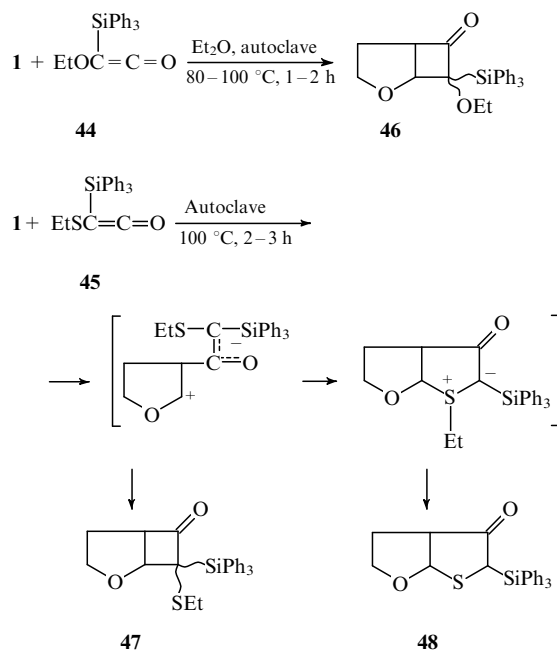
The reaction of the enol ether **1** with ketene **35** results in the formation of adduct **36** (yield 80%), treatment of which with toluene-*p*-sulfonic acid gives compound **37** in 70% yield.²⁰



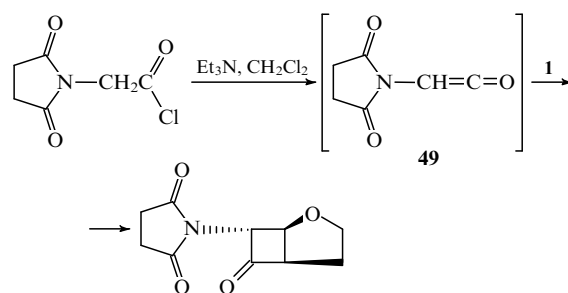
Various heterocyclic compounds have been synthesised based on 7-chloro-7-phenyl-2-oxabicyclo[3.2.0]heptan-6-one **38**, which is formed in 75% yield upon [2 + 2]-cycloaddition of the enol ether **1** to chloro(phenyl)ketene **39**. For example, a mixture of lactones **40** and **41** was obtained in 45% overall yield, and bicyclic lactone **42** was prepared as a mixture of *cis*- and *trans*-isomers in a ratio of 1 : 1.6.



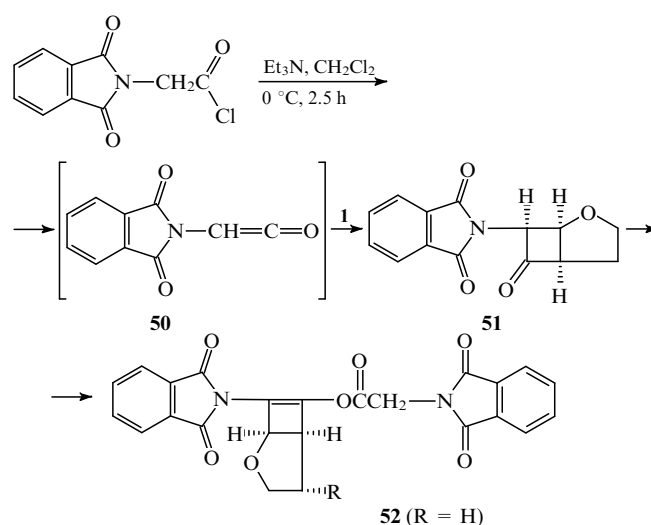
The reactions of the enol ether **1** with ethoxy(triphenylsilyl)ketene **44** and its sulfur-containing analogue **45** follow essentially dissimilar pathways. Whereas the interaction of the enol ether **1** with the ketene **44** affords only the [2 + 2]-cycloaddition product **46** (yield 85%),²² in the case of the ketene **45**, two compounds are formed: adduct **47** (yield 5%) and 7-triphenylsilyl-2-oxa-8-thiabicyclo[3.3.0]octan-6-one **48** (yield 14%).²³



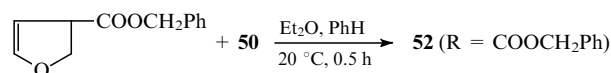
Ketene **49** arising upon treatment of succinimidoacetyl chloride with triethylamine enters into the [2 + 2]-cycloaddition reaction with the enol ether **1** leading to 7-succinimido-2-oxabicyclo[3.2.0]heptan-6-one.²⁴



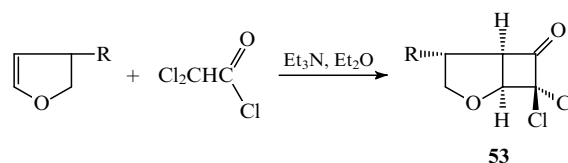
Two compounds have been obtained in the reaction of 2,3-dihydrofuran **1** with ketene **50**, prepared by treating phthalimidoacetyl chloride with triethylamine, namely, compound **51** resulting from [2 + 2]-cycloaddition (yield 40%) and 2-oxabicyclo[3.2.0]hept-6-ene derivative **52** ($\text{R} = \text{H}$, yield 7%) arising *via* acylation of the enol form of the adduct **51** with the initial acyl chloride.²⁵



The reaction of 3-benzyloxycarbonyl-2,3-dihydrofuran with ketene **50** affords only compound **52** ($\text{R} = \text{COOCH}_2\text{Ph}$, yield 28%).²⁵



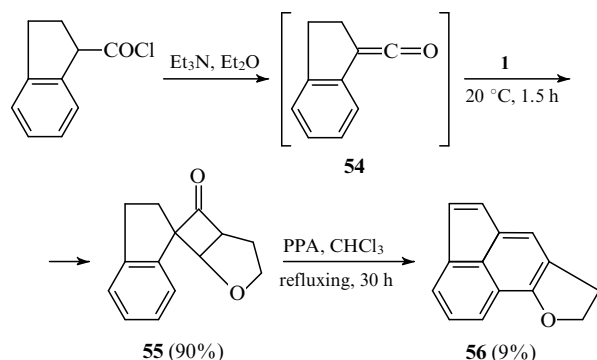
As expected, the interaction of the enol ether **1** or 3-benzyloxycarbonyl-2,3-dihydrofuran with dichloroacetyl chloride in the presence of triethylamine gives only the products of [2 + 2]-cycloaddition **53**.²⁶



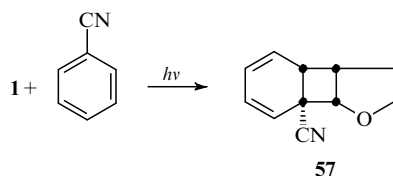
R	T / °C	Time / h	Yield (%)
H	20	2.5	55
COOCH_2Ph	0	1	53

Ketene **54** generated from indane-1-carboxylic acid chloride by treating it with triethylamine under an inert atmosphere has been made to react *in situ* with the enol ether **1** according to the [2 + 2]-cycloaddition route; this has led to the spiro-compound **55**.

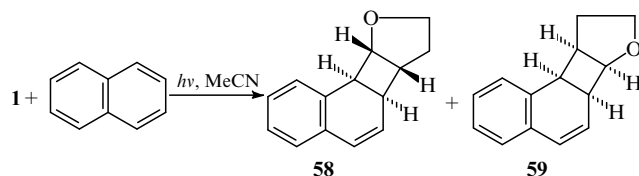
Prolonged refluxing of the cycloaddition product **55** in chloroform in the presence of polyphosphoric acid results in its recyclisation yielding compound **56**.²⁷



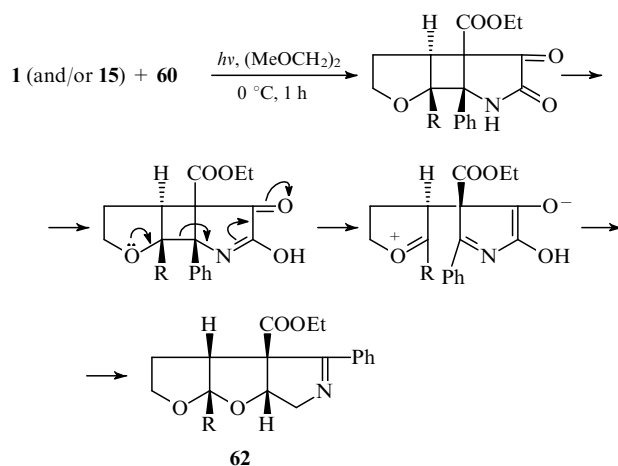
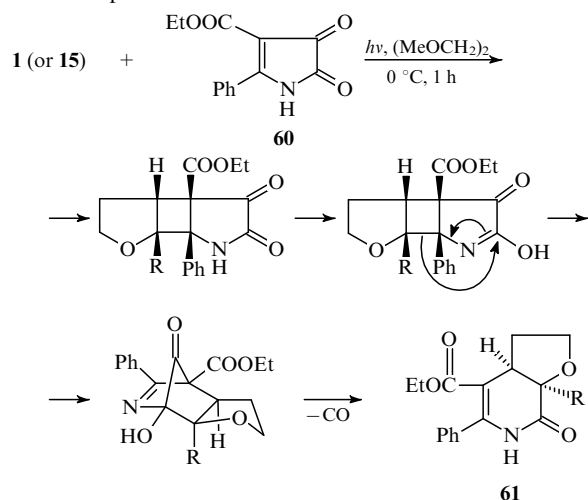
When the enol ether **1** and benzonitrile are irradiated with light from a 70-W low-pressure mercury lamp through a quartz filter under an inert atmosphere, [2 + 2]-cycloaddition reaction takes place giving rise to 1-cyano-3-oxatricyclo[5.4.0.0^{2,6}]undeca-8,10-diene **57** in 20% yield.²⁸



Gilbert *et al.*²⁹ managed to accomplish [2 + 2]-cycloaddition of the enol ether **1** to naphthalene by irradiating a mixture of the initial compounds with the light from a 125-W medium-pressure mercury lamp. Adducts **58** and **59** were obtained in this way in a low overall yield (5%).²⁹

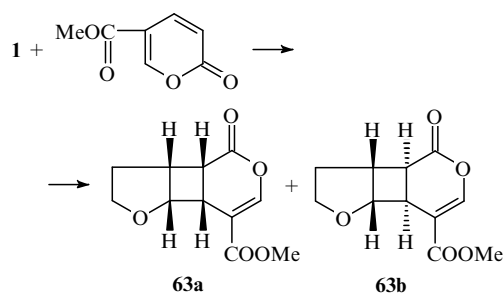


When compound **60** is exposed to the radiation of a high-pressure mercury lamp in the presence of compound **1** or **15**, a mixture of two products **61** and **62** is obtained in each case. The researchers³⁰ believe that the compounds **61** are formed *via* an intermediate *endo*- π -complex, whereas the compounds **62** arise *via* an *exo*- π -complex.

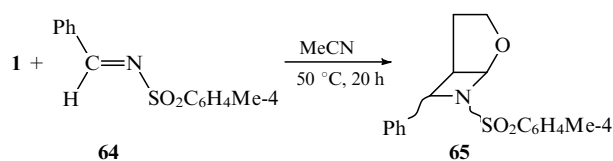


R	Yield (%)	
	61	62
H	2	8
Me	14	77

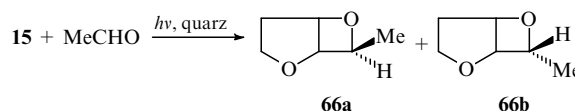
When the enol ether **1** is made to react with methyl 2-pyrone-5-carboxylate, two diastereomeric products of [2 + 2]-cycloaddition, **63a** and **63b**, are formed.³¹



At 50 °C and under a pressure of 12 kbar, *N*-tosylimine **64** undergoes [2 + 2]-cycloaddition to the enol ether **1**, which affords adduct **65** as a mixture of *cis, cis*-, *trans, cis*-, and *cis, trans*-isomers in 80% overall yield; the individual *cis, cis*-isomer was isolated from this mixture in a yield of 35%.³²

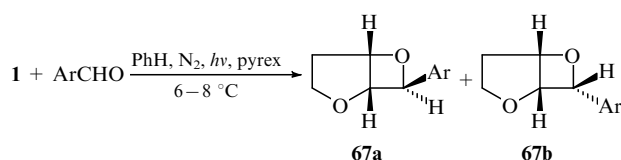


The irradiation of 5-methyl-2,3-dihydrofuran **15** and acetaldehyde with the light from a medium-pressure mercury lamp results in the formation of compound **66** as a mixture of isomers **66a** (yield 36%) and **66b** (yield 27%).³³



Japanese investigators³⁴ carried out [2 + 2]-cycloaddition of 2,3-dihydrofuran to benzaldehyde by irradiating the initial compounds with a high-pressure mercury lamp (450 W) under a nitrogen atmosphere at 0 °C for 6 h. They obtained a mixture of (1*SR*, 5*RS*, 7*SR*)- and (1*SR*, 5*RS*, 7*RS*)-7-phenyl-2,6-dioxabicyclo[3.2.0]heptanes (**67a,b**, Ar = Ph).

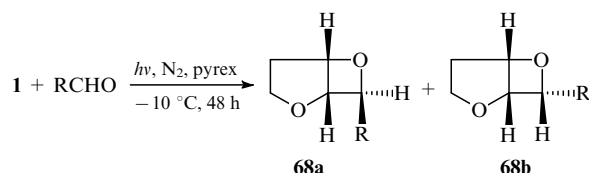
When this reaction has been carried out on exposure to the radiation of a 150-W high-pressure mercury lamp, the ratio of the isomers **67a** and **67b** has been found to depend on the nature of the aromatic aldehyde used.^{35, 36}



Ar	Time / h	Yield (%)	Ratio 67a : 67b
Ph	11	50	7 : 1
2-MeC ₆ H ₄	16	94	15 : 1
2,4,6-Me ₃ C ₆ H ₂	8.5	97	20 : 1
2-Me-4,6-(Bu ^t) ₂ C ₆ H ₂	24	28	20 : 1

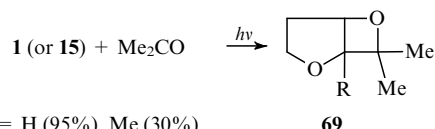
The rate and diastereoselectivity of the cycloaddition reaction involving the enol ether **1** were found to be higher than those in the case of cyclopentene.³⁵

The diastereoselectivity of [2 + 2] cycloaddition of the enol ether **1** to aromatic aldehydes is completely reversed when the electronic configuration of the excited triplet form [3(*nπ**) – 3(*ππ**)] changes: in the case of 2,4,6-trimethylbenzaldehyde, the diastereomer **68a** is formed predominantly, while in the case of aldehydes of the naphthalene series, the diastereomer **68b** predominates.³⁷



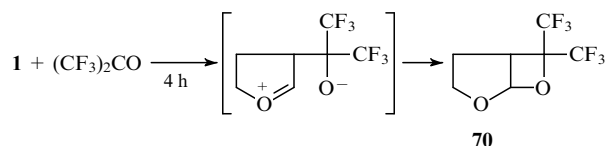
R	Yield (%)	Ratio 68a : 68b
Me	76	55 : 45
2,4,6-Me ₃ C ₆ H ₂	97	2 : 98
α-Naphthyl	55	98 : 2
β-Naphthyl	53	98 : 2

2,6-Dioxabicyclo[3.2.0]heptane derivatives **69** have been synthesised by [2 + 2]-cycloaddition of the enol ether **1** or **15** to acetone occurring on exposure to radiation of a medium-pressure mercury lamp.³³



R = H (95%), Me (30%).

A similar reaction involving hexafluoroacetone affords adduct **70**. It has been found that the reaction temperature and the nature of the solvent exert a substantial influence on the selectivity of the process, on the degree of conversion, and on the yield of the adduct **70**.³⁸



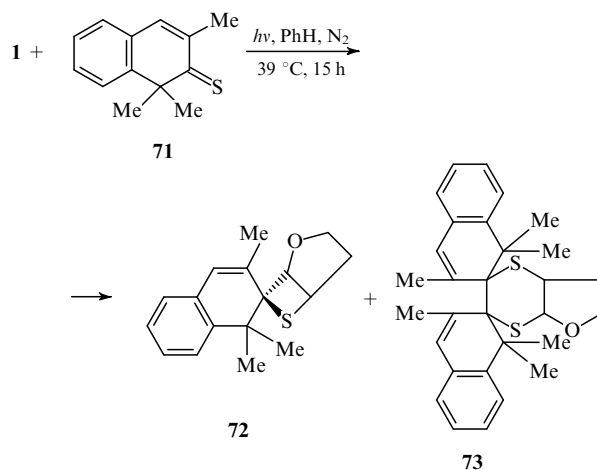
A. Temperature dependence of the selectivity and the yield of **70**.

T / °C	Yield (%)	Selectivity (%)	Conversion of 1 (%) (in heptane)
–5	39	39	100
–10	45	46	99
–15	56	75	74
–20	57	81	71
–62 (6 h)	62	62	100

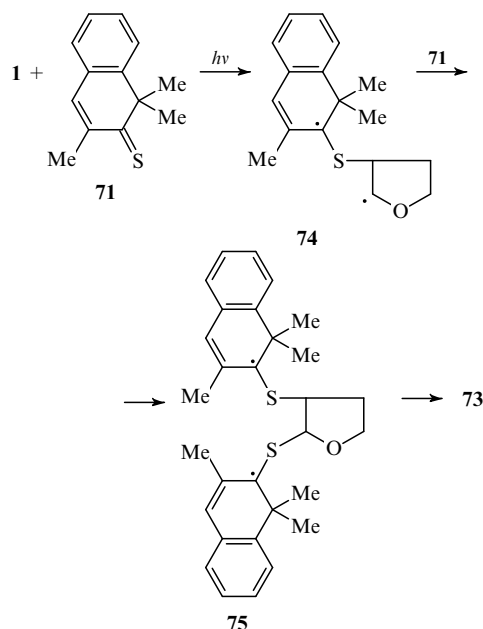
B. Solvent dependence of the selectivity and the yield of **70**.

Solvent	Yield (%)	Selectivity (%)	Conversion of 1 (%)
Et ₂ O	24	70	34
CHCl ₃	27	27	100
PhMe	50	51	98
Heptane	57	81	71

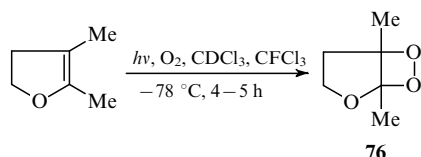
The irradiation of a mixture of the enol ether **1** and 1,3,3-trimethyl-1,2-dihydronaphthalene-2-thione **71** with an RPR lamp ($\lambda = 350 \text{ nm}$) has led to two compounds: [2 + 2]-cycloaddition product **72** and compound **73** resulting from the interaction of one molecule of the enol ether **1** with two molecules of the initial naphthalene derivative **71**.³⁹



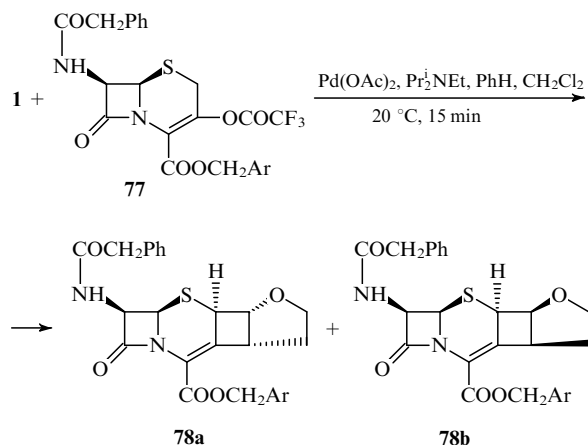
The formation of the compound **73** was explained³⁹ in terms of a scheme involving the generation of biradicals **74** and **75**.



4,5-Dimethyl-2,3-dihydrofuran has been photooxidised by irradiation with a filtered light ($\lambda = 500\text{--}595 \text{ nm}$) of a 150-W lamp under an oxygen atmosphere in the presence of tetraphenylporphyrin or Bengal Rose. Among other products, 1,5-dimethyl-2,6,7-trioxabicyclo[3.2.0]heptane **76**, which can formally be regarded as resulting from the [2 + 2]-cycloaddition of oxygen to the double bond, is formed in 48% yield.



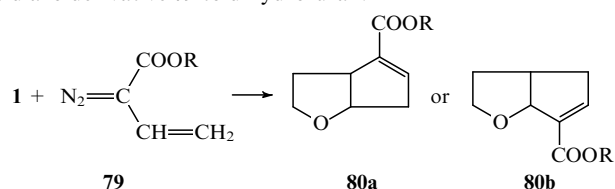
Cyclocondensation of the enol ether **1** with cephalosporin **77** in the presence of palladium acetate and ethyldiisopropylamine has led to compound **78**, which was separated into two isomers **78a** and **78b** (overall yield 73%, ratio of isomers 1.8 : 1).⁴¹



Ar = C₆H₄OMe-4.

3. [3 + 2]-Cycloaddition

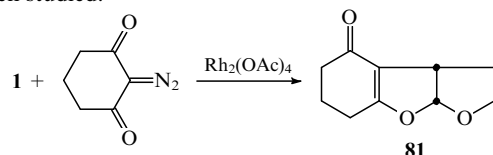
Esters of 2-diazobut-3-enoic acid **79** decompose in the presence of various catalysts to give the corresponding carbenes; however, the primary products arising upon the addition of these carbenes to the double bond of 2,3-dihydrofuran **1** undergo a rearrangement affording regioisomers of 2-oxabicyclo[3.3.0]octene, which contain the ester group in the 6-position (**80a**) or in the 8-position (**80b**)^{42,43} and are formally the products of [2 + 3]-cycloaddition of the diazo derivative **79** to dihydrofuran.



R	Catalyst	Solvent	Yield (%)		Ref.
			80a	80b	
Me	Rh ₂ (OC ₈ H ₁₇) ₄ Et ₂ AlCl	Pentane	66	—	42
	Rh ₂ (OAc) ₄	CH ₂ Cl ₂	—	40–42	42, 43

2,3-Dihydrofuran **1** reacts in a similar way with some other diazo compounds.

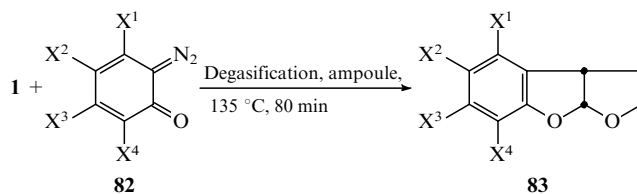
The influence of the reaction conditions on the yield of the product **81** resulting from the interaction of the enol ether **1** with 2-diazocyclohexane-1,3-dione in the presence of Rh₂(OAc)₄ has been studied.⁴⁴



When the reaction is carried out without a solvent with boiling (2 h) or at 25 °C (4 h), compound **81** is formed in 84% yield. The nature of the solvent used in this reaction (25 °C, 24 h) has a substantial influence on the yield of the compound **81**.

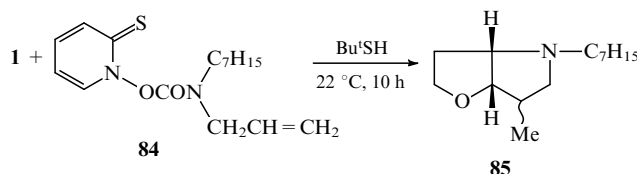
Solvent	C ₆ H ₅ F	THF	PhH	CH ₂ Cl ₂	MeCN
Yield of 81 (%)	70	61	48	43	20

Thermal cyclocondensation of the enol ether **1** with diazo compounds **82** has given rise to furo[2.3-*b*]-2,3-dihydrobenzofuran derivatives **83** (yields 45%–56%).⁴⁵

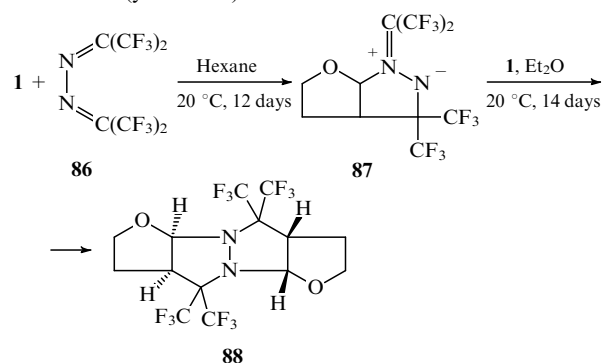


X ¹	X ²	X ³	X ⁴
H	Cl	H	Cl
OMe	Cl	H	Cl
Br	H	Br	H

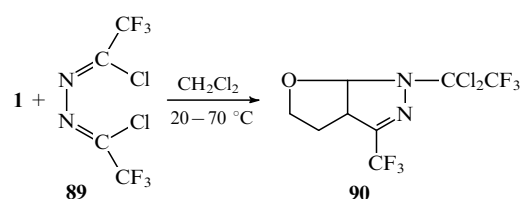
The reaction of the enol ether **1** with carbamate **84**, containing an allyl radical, in the presence of 2-methylpropane-2-thiol gave a mixture of *exo*- and *endo*-isomers of adducts **85** (in a ratio of 1 : 3) in 52% overall yield.⁴⁶



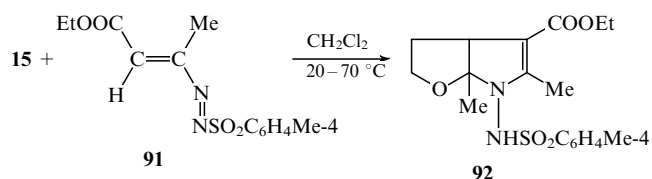
Perfluorinated heterodiene **86** reacts with the enol ether **1** at 20 °C to give the stable bipolar ion **87** in a yield of 48%. The latter undergoes [3 + 2]-cycloaddition to a further molecule of the enol ether **1**, which affords a bis-adduct, namely, 7,7,14,14-tetrakis-(trifluoromethyl)-3,10-dioxo-1,8-diazatetracyclo[6.6.0.0.2⁶0^{9,13}]-tetradecane **88** (yield 17%).⁴⁷



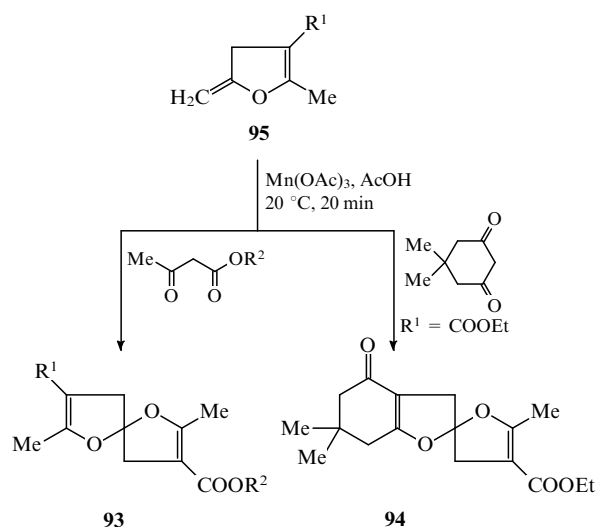
The [3 + 2]-cycloaddition of 2,3-dihydrofuran **1** to 1,4-dichloro-1,4-bis(trifluoromethyl)-2,3-diazabuta-1,3-diene **89** is accompanied by a rearrangement of this dichloroazine and yields compound **90** resulting from the 1,3-dipolar cycloaddition of the arising nitrilimine CF₃C=N⁺–N[–]CCl₂CF₃.⁴⁸



Clarke *et al.*⁴⁹ have suggested that the interaction of the compound **91** with 5-methyl-2,3-dihydrofuran **15** leads to the furanopyrrole derivative **92** (yield 35%). Apparently, this process also involves the intermediate formation of the corresponding nitrilimine.

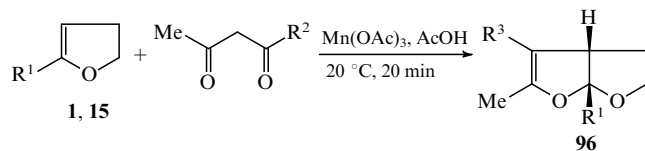


The spiro-compounds **93** and **94**, containing each two dihydrofuran fragments, are formed in the condensation of dihydrofuran derivatives **95** with acetoacetates or with 5,5-dimethylcyclohexane-1,3-dione in the presence of manganese(III) acetate under an inert atmosphere.⁵⁰



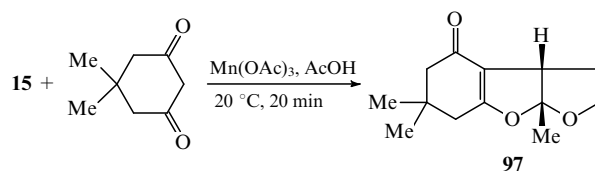
R^1	R^2	Yield 93 (%)
COOEt	Et	37
COOEt	CH_2Ph	40
SO_2Ph	Et	26

Enol ethers **1** or **15** react with acetoacetates or with pentane-2,4-dione under the same conditions to give compounds with a different structure — 1,5-dioxabicyclo[3.3.0]octane derivatives **96**.⁵⁰

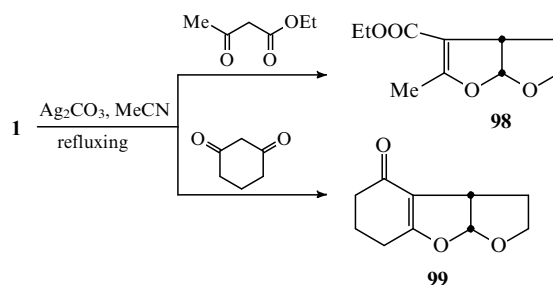


R^1	R^2	R^3	Yield 96 (%)
Me	OEt	COOEt	51
H	OEt	COOEt	53
H	OCH_2Ph	COOCH_2Ph	56
H	Me	MeCO	26

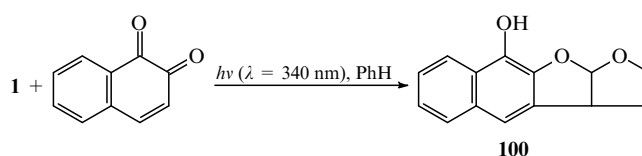
Tricyclic compound **97** has been obtained in 40% yield by cyclocondensation of the enol ether **15** with 5,5-dimethylcyclohexane-1,3-dione.⁵⁰



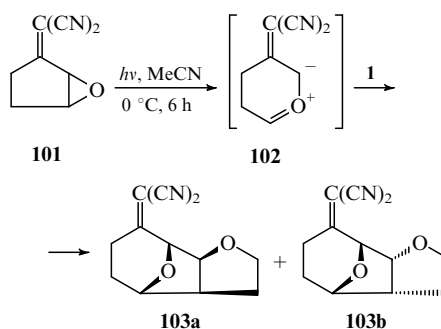
Kraus *et al.*⁵¹ showed that the cyclocondensation of the compound **1** with esters of oxoacids or with cyclic diketones can be carried out in the presence of silver carbonate in boiling acetonitrile under an inert atmosphere. For example, compounds **98** (yield 50%) and **99** (yield 60%–76%) were prepared from the enol ether **1** and ethyl acetoacetate and cyclohexane-1,3-dione, respectively.



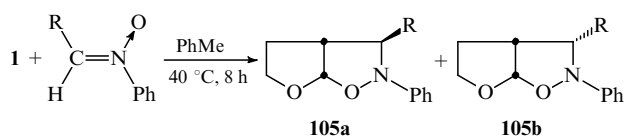
The yield of compound **100** resulting from the photochemical reaction (high-pressure mercury lamp) of 2,3-dihydrofuran **1** with 1,2-naphthoquinone depends markedly on the polarity of the solvent in which the process is conducted. In fact, in nonpolar benzene ($D = 0.00$), the yield of the compound **100** is only 6%, whereas in acetonitrile ($D = 3.37$), the yield reaches 58%.⁵²



When epoxide **101** is irradiated with a low-pressure mercury lamp (60 W, $\lambda = 254\text{ nm}$) through a quartz filter under an inert atmosphere, it gives rise to carbonylylide **102**, which enters into 1,3-dipolar cycloaddition to 2,3-dihydrofuran **1** to give adducts **103a,b** as pairs of diastereomers (yields 21% and 5%, respectively).⁵³

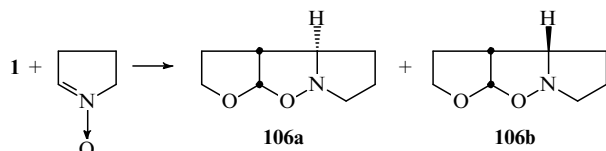


Reactions of [3 + 2]-cycloaddition of various 1,3-dipoles to 2,3-dihydrofurans have been studied fairly well. For example, 1,3-dipolar cycloaddition of the enol ether **1** to nitrones **104** proceeds according to the 'head-to-head' type and yields a mixture of *endo*- and *exo*-isomers **105a,b**.⁵⁴ The ratio of the isomers depends on the nature of the group R in the nitrone.

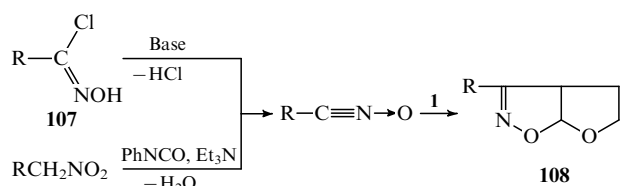


R	Ratio 105a : 105b
PhCO	52:48
Ph	22:78

Cycloaddition of the enol ether **1** to pyrroline *N*-oxide occurs stereoselectively; the reaction products consist predominantly of the diastereomer **106a** (yield 91%), only a small amount of the diastereomer **106b** being formed (yield 3%).⁵⁵

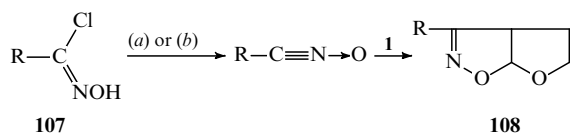


The first study devoted to the 1,3-dipolar addition of *N*-oxides of aliphatic, aromatic, and heterocyclic carboxylic acid nitriles to 2,3-dihydrofuran was published in 1962.⁵⁶ The nitrile *N*-oxides were generated by two methods: by treating hydroximoyl chlorides **107** with bases and by dehydration of primary nitro compounds through the action of phenyl isocyanate in the presence of triethylamine. Nitrile *N*-oxides were introduced *in situ* into the reaction with 2,3-dihydrofuran. The cycloaddition occurred according to the 'head-to-head' type and gave adducts **108**.



The conditions under which the nitrile *N*-oxides were generated and the yields of the adducts **108** are presented in Table 1.

Some 3a,4,5,6a-Tetrahydrofuro[2,3-*d*]isoxazoles **108** containing substituents in the 3-position have been synthesised by the cycloaddition of the enol ether **1** to the *N*-oxides of aliphatic carbonitriles, prepared by treatment of hydroxamic acid chlorides **107** with sodium carbonate in water (*a*)⁵⁷ or with triethylamine in ether (*b*).^{58–61}

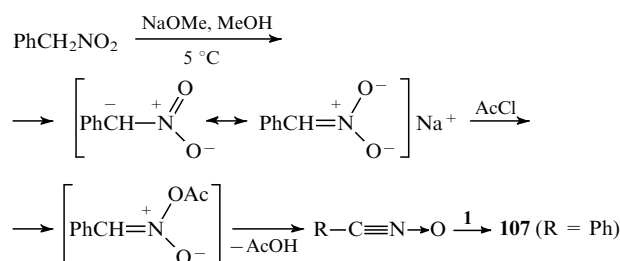


R	Yield (%)	Ref.
CN	25	57
COOEt	51	58, 59
Me	—	59
Ph	—	60
2,4-Cl ₂ C ₆ H ₃	—	61

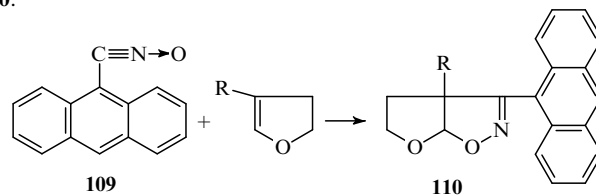
Harada *et al.*⁶² described another method for the generation of benzonitrile *N*-oxide, which involves successive treatment of phenylnitromethane with sodium methoxide and acetyl chloride, and proposed a mechanism for this process. The resulting *N*-oxide was introduced *in situ* into the cycloaddition reaction with 2,3-dihydrofuran **1**.

Table 1. Conditions of reactions of 2,3-dihydrofuran **1** with nitrile *N*-oxides and yields of adducts **108**.

Substrate	Reaction conditions	Yield of 108 (%)
PhC(Cl)=NOH	NaOH, H ₂ O, 0 °C, 25 min	40
C(Cl)=NOH	NaOH, H ₂ O, 20 °C, 1 h	65
C(Cl)=NOH	Et ₃ N, Et ₂ O, EtOCH ₂ CH ₂ OEt, 20 °C, 40 min	42
C(Cl)=NOH	Et ₃ N, Et ₂ O, EtOCH ₂ CH ₂ OEt, 20 °C, 40 min	59
PhC(O)C(Cl)=NOH	Et ₂ O, EtOCH ₂ CH ₂ OEt, pH 8 (citrate-phosphate buffer), 5 °C, 15 min	67
MeCH ₂ NO ₂	Et ₃ N, PhNCO, PhH, refluxing, 1 h	66
EtCH ₂ NO ₂	Et ₃ N, PhNCO, PhH, refluxing, 1 h	67
PrCH ₂ NO ₂	Et ₃ N, PhNCO, PhH, refluxing, 1 h	71
EtOCOCH ₂ NO ₂	Et ₃ N, PhNCO, PhH, 35 °C, 1 h	59
MeOCO(CH ₂) ₃ NO ₂	Et ₃ N, PhNCO, PhH, refluxing, 1 h	66

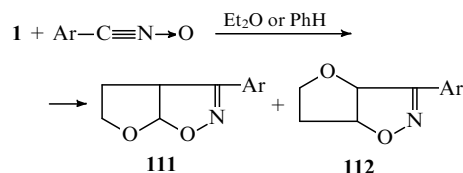


The 1,3-dipolar cycloaddition of anthracene-9-carbonitrile *N*-oxide **109** to 2,3-dihydrofuran **1** or to 4-methoxycarbonyl-2,3-dihydrofuran has been used to prepare the corresponding adducts **110**.⁶³



R = H (61%), COOMe (31%).

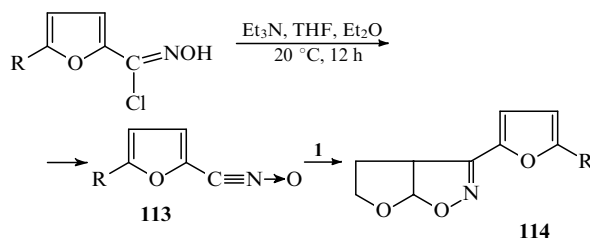
Thorough investigation of 1,3-dipolar cycloaddition reactions involving 2,3-dihydrofuran **1** and benzonitrile and 2,4,6-trimethylbenzonitrile *N*-oxides has shown that these reactions are highly regioselective and that the 'head-to-head' coupling giving adducts **111** is the main reaction route. Only slight amounts of products **112** resulting from the 'head-to-tail' addition were isolated.⁶⁴



Ar	Ratio 111 : 112
Ph	99.4 : 0.6
2,4,6-Me ₃ C ₆ H ₂	99.5 : 0.5

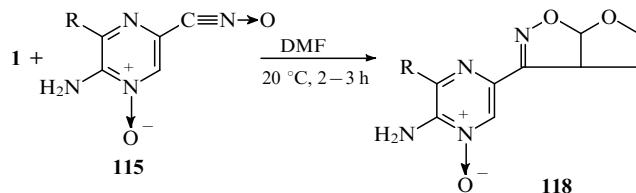
The same investigators⁶⁴ also found that the enol ether **1** reacts with nitrile *N*-oxides 1.8 times more rapidly than cyclopentene. They attributed this result to the resonance interaction of the double bond with the electron pair on the oxygen atom, which leads to an increase in the electron density on the carbon atom in the 4-position of the enol ether and to an increase in the electrophilicity of the double bond.

The carbonitrile *N*-oxides of the furan series **113** react with the enol ether **1** stereospecifically to give adducts **114** (yields 71%–85%).⁶⁵

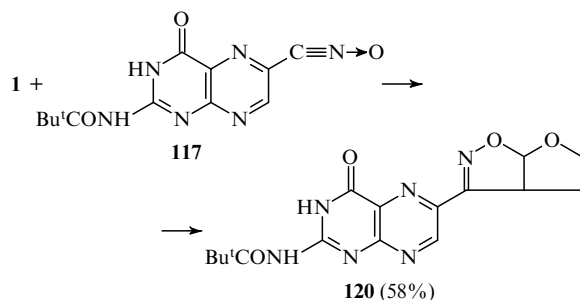
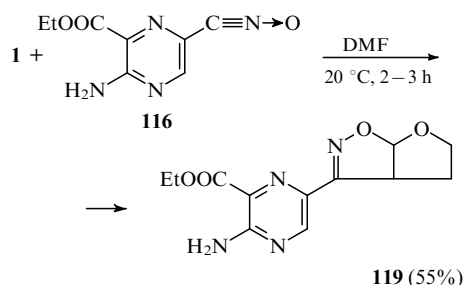


R = H, NO₂, 4-O₂NC₆H₄.

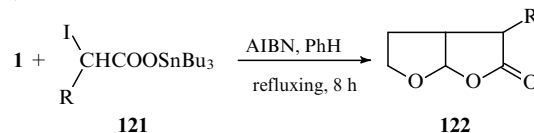
The 1,3-dipolar cycloaddition of 2,3-dihydrofuran **1** to the carbonitrile *N*-oxides of the pyrazine series (**115**, **116**) or of the pteridine series (**117**) has made it possible to synthesise adducts **118**, **119**, or **120**, respectively.⁶⁶ The reactions were carried out under an inert atmosphere.



R = COOEt (60%), CN (10%).



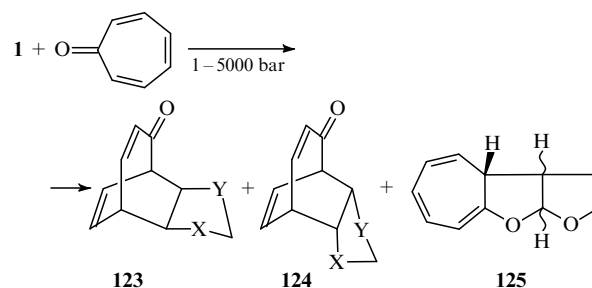
The enol ether **1** enters into cyclocondensation with tributylstannyl iodoacetate or α -iodopropionate **121** in the presence of azobisisobutyronitrile (AIBN) in boiling benzene to give 2,8-dioxabicyclo[3.3.0]octan-3-one **122** (R = H, yield 78%) or its 4-methyl-derivative **122** (R = Me, yield 72%). The latter compound is formed as a mixture of diastereomers in a ratio of 1 : 1.^{67,68}



R = H, Me.

4. [4 + 2]-Cycloaddition

Two [4 + 2]-cycloaddition products as mixtures of two isomers (**123a,b** and **124a,b**) and [3 + 2]-cycloaddition product **125** have been obtained by the reaction of the enol ether **1** with tropolone under an elevated pressure. The product ratio (**123** + **124**) : **125** is pressure-dependent.⁶⁹

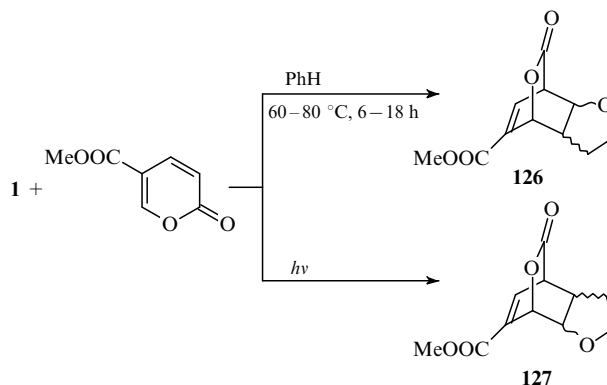


123a: X = O, Y = CH₂;

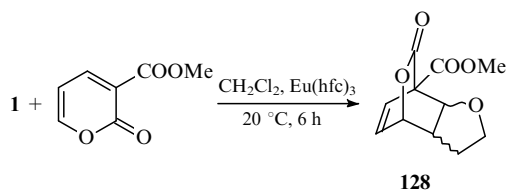
123b: X = CH₂, Y = O.

Published studies indicate that [4 + 2]-cycloaddition of 2,3-dihydrofuran or its derivatives to esters of 2-pyronecarboxylic acids can be carried out under irradiation with actinic light, in the presence of catalysts, or it can be induced thermally.

The thermal condensation of the enol ether **1** with methyl 2-pyrone-5-carboxylate and the condensation induced by UV radiation afford different products. When the initial compounds were kept in benzene at 60–80 °C, methyl 9-oxo-3,8-dioxatricyclo[5.2.2.0^{2,6}]undec-10-ene-11-carboxylate **126** was obtained as a mixture of two isomers (*endo*, yield 25% and *exo*, yield 38%),⁷⁰ whereas the photochemical reaction, in which the orientation of the addends was opposite, afforded methyl 8-oxo-3,9-dioxatricyclo[5,2,2,0^{2,6}]undec-10-ene-10-carboxylate **127**.³¹

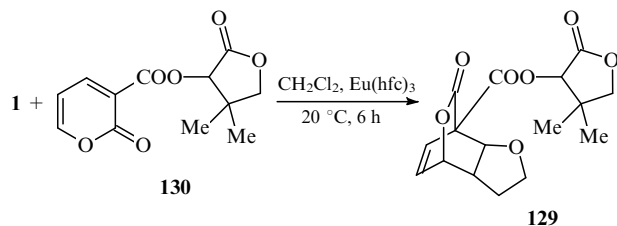


In the presence of lanthanide shift-reagents, the cycloaddition of enol ether **1** to methyl 2-pyrone-3-carboxylate occurs smoothly give products in high yields. When the reaction is carried out at 20 °C in the presence of Eu(hfc)₃, adduct **128** can be obtained in a yield of 93%–96%.^{71–73} In the reaction carried out at 0 °C for 0.5 h under an argon atmosphere in the presence of Yb(OTf)₃, the yield of the product was 93%.⁷⁴



However, the thermal reaction (DMSO , $70\text{--}80^\circ\text{C}$) in the absence of a shift-reagent afforded the adduct **128** in a yield of only 41%.⁷¹

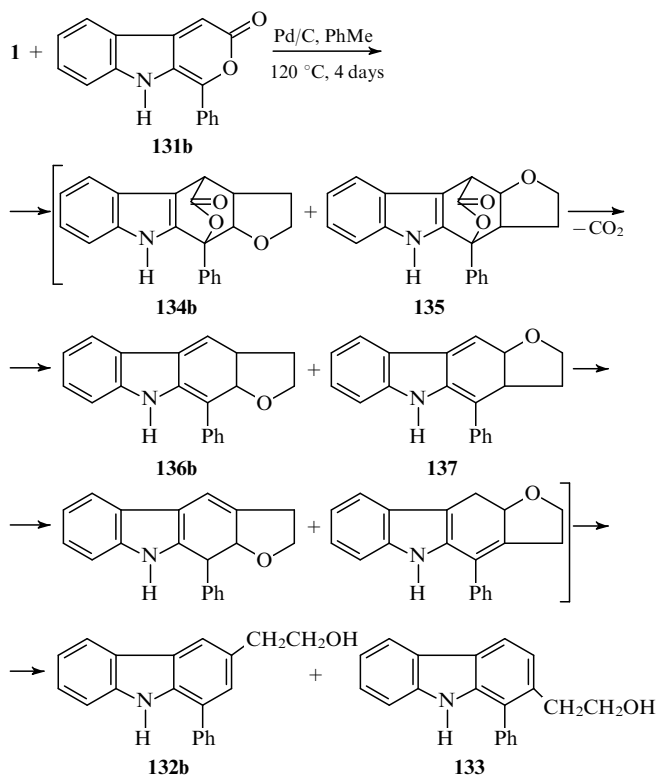
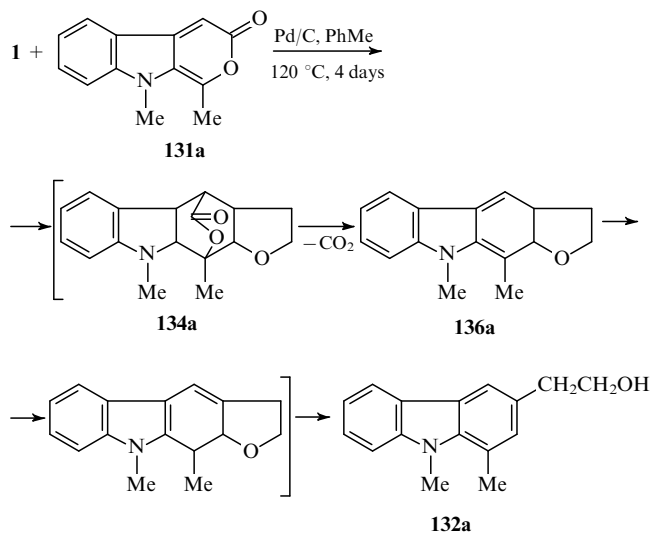
Compound **129** is formed in 96% yield upon the [4+2]-cycloaddition of the enol ether **1** to the 2-pyrone derivative **130** in the presence of $\text{Eu}(\text{hfc})_3$.⁷⁴



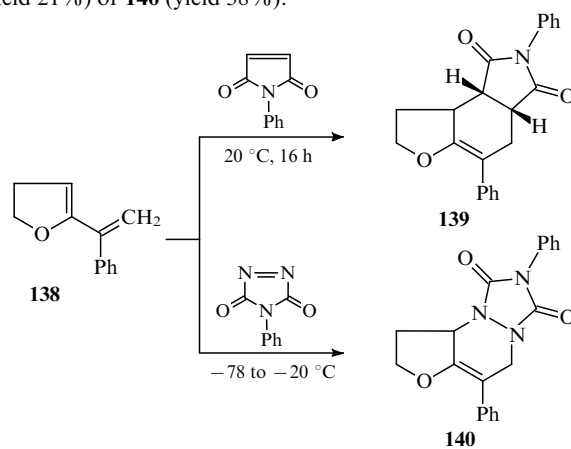
The kinetics of the [4+2]-cycloaddition of various unsaturated compounds to dimethyl 1,2,4,5-tetrazine-3,6-dicarboxylate have been studied.⁷⁵ It was found that the reaction involving the enol ether **1** occurs 180 times faster than that with 2,3-dihydropyran and 6 times faster than the reaction involving ethyl vinyl ether or cyclopentene.

Heating of the enol ether **1** with pyranono[3,4-*b*]indole **131a,b** in the presence of Pd/C in a sealed tube has given carbazole derivatives **132a** (from **131a**, yield 58%) or a mixture of isomers **132b** and **133** (from **131b**, yield 85%, ratio 5 : 4).

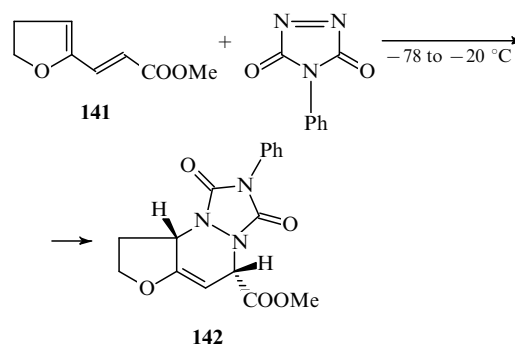
Evidently, the first stage of this process is [4+2]-cycloaddition, which is not regioselective in the case of the phenyl-substituted derivative **131b**. The resulting adducts **134a,b** and **135** lose a CO_2 molecule and thus generate indole-2,3-quinodimethane derivatives **136a,b** and **137**, which undergo a 1,5-sigmatropic H-shift, which leads (after cleavage of the tetrahydrofuran ring) to the final products **132a,b** or **133**.⁷⁶



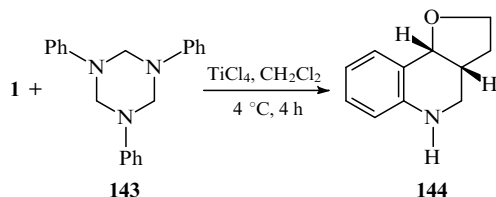
The Diels–Alder condensation of the vinyl-substituted dihydrofuran **138** with *N*-phenylmaleimide or with 4-phenyl-1,2,4-triazoline-3,5-dione has given the corresponding adducts **139** (yield 21%) or **140** (yield 38%).⁷⁷



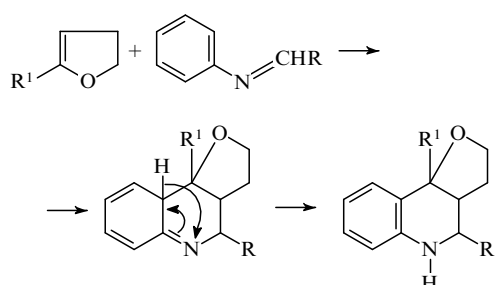
The [4+2]-cycloaddition of methyl (*E*)-3-(2,3-dihydro-5-furyl)acrylate **141** to 4-phenyl-1,2,4-triazoline-3,5-dione is highly stereoselective and affords almost exclusively the *trans*-isomer of the adduct **142** (*E* : *Z* ≥ 95 : 1, yield 88%).⁷⁷



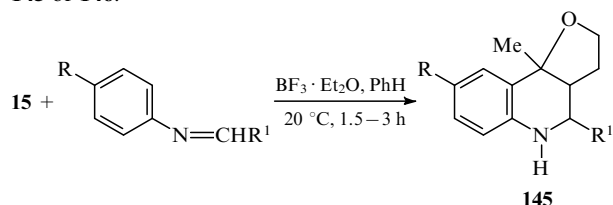
The cyclotrimer of *N*-methylethaniline **143** reacts with 2,3-dihydrofuran in the presence of titanium(IV) chloride giving rise to 2,3,3a β ,4,5,9b β -hexahydrofuro[3,2-*c*]quinoline **144** (yield 16.8%).⁷⁸



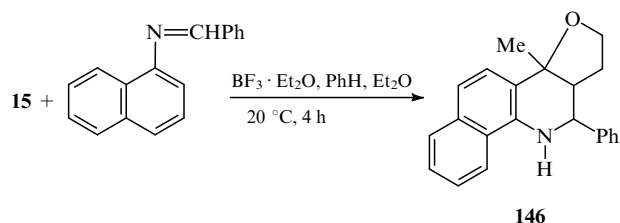
The first stage of the interaction of enol ethers with azomethines is obviously the [4+2]-cycloaddition involving the phenyl substituent. This is followed by the 1,3-shift of hydrogen, which restores the aromatic system and results in the formation of tetrahydroquinoline derivatives.



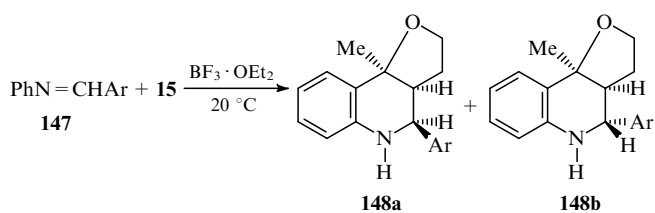
In the first study⁷⁹ devoted to the interaction of enol ethers with azomethines, the reaction of 5-methyl-2,3-dihydrofuran **15** with azomethines of the general formula $\text{ArN}=\text{CHR}_1$ in the presence of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ was studied. The authors reported that this process is exothermic and is completed at ambient temperature. The reaction proceeds stereospecifically and affords compounds **145** or **146**.



R	R ¹	Yield (%)
H	Ph	81.3
MeO	Ph	70.3
H		61.5

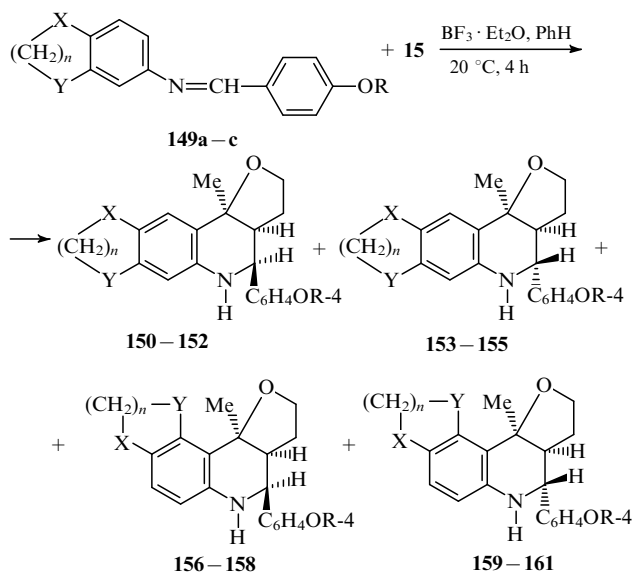


However, more recently,⁸⁰ it was shown that the reaction of the enol ether **15** with azomethines **147** is non-stereospecific and results in the formation of mixtures of diastereomers **148a,b** in a ratio of 1 : 1.



$\text{Ar} = \text{Ph}, 2\text{-ClC}_6\text{H}_4$.

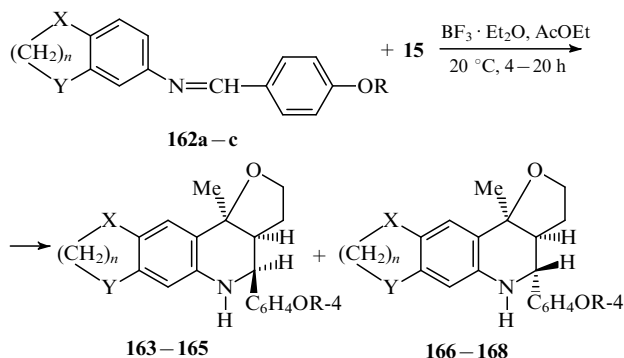
When the enol ether **15** reacts with the azomethines $\text{PhN}=\text{CHC}_6\text{H}_4\text{NO}_2$ in benzene in the presence of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ at 20 °C for 4 h, a mixture consisting of equal amounts of *cis*-**148a** and *trans*-*dl*-2,3,3a,4,5,9b-hexahydro-9b-methyl-4-(*o*-nitrophenyl)furo[3,2-*c*]quinoline **148b** ($\text{Ar} = \text{C}_6\text{H}_4\text{NO}_2$) is also formed.⁸¹ A detailed study of the reactions of the enol ether **15** with azomethines of the general formula $\text{ArN}=\text{CHC}_6\text{H}_4\text{OR}$ **149a–c** has shown that, depending on the nature of Ar, the process yields either one or two pairs of diastereomers.



149a, **150**, **153**, **156**, **159**: $\text{X} = \text{Y} = \text{O}$, $n = 2$, $\text{R} = \text{Me}$;
149b, **151**, **154**, **157**, **160**: $\text{X} = \text{NAc}$, $\text{Y} = \text{CH}_2$, $n = 2$, $\text{R} = \text{H}$;
149c, **152**, **155**, **158**, **161**: $\text{X} = \text{Y} = \text{CH}_2$, $n = 1$, $\text{R} = \text{Me}$.

For example, two pairs of diastereomers are formed in the reactions of dihydrofuran **15** with each of compounds **149a**,⁸² **149b**,⁸³ or **149c**. The overall yield of reaction products **150**, **153**, **156**, and **159** is 15%, that of **151**, **154**, **157**, and **160** is 48%, and that of **152**, **155**, **158**, and **161** is 64%.

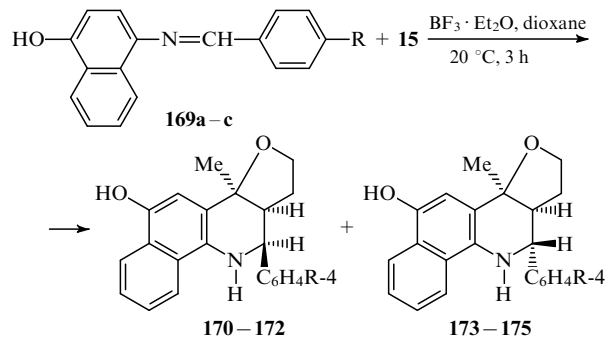
On the other hand, the reactions between the enol ether **15** and the Schiff's bases **162a**,⁸² **162b**,⁸³ or **162c**⁸³ resulted in the formation of only one diastereomer pair.



162a, **163**, **166**: $\text{X} = \text{Y} = \text{O}$, $n = 1$, $\text{R} = \text{Me}$;
162b, **164**, **167**: $\text{X} = \text{CH}_2$, $\text{Y} = \text{NAc}$, $n = 1$, $\text{R} = \text{H}$;
162c, **165**, **168**: $\text{X} = \text{NAc}$, $\text{Y} = \text{CH}_2$, $n = 1$, $\text{R} = \text{H}$.

The overall yield of the two isomers **163** and **166** was 45%, that of the compounds **164** and **167** was 48%, and the yield of **165** and **168** was 45%.

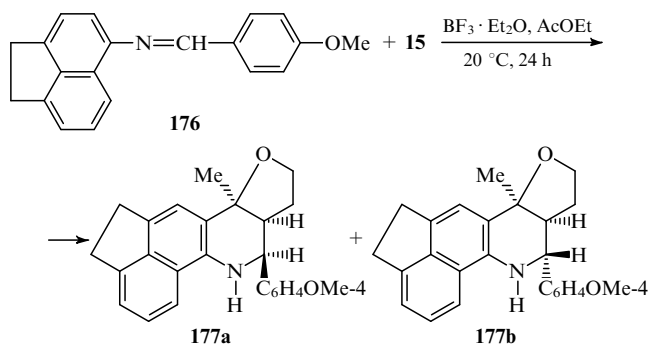
Similar stereochemical results have been obtained in another study⁸⁴ of the interaction of the enol ether **15** with Schiff's bases **169a,b** and **176**.



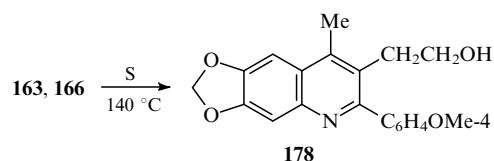
169a, 170, 173: R = H; **169b, 171, 174:** R = OH; **169c, 172, 175:** R = OMe.

The overall yield of the diastereomers **170** and **173** was 81%, that of **171** and **174** was 47%, and the yield of **172** and **175** was 46%.

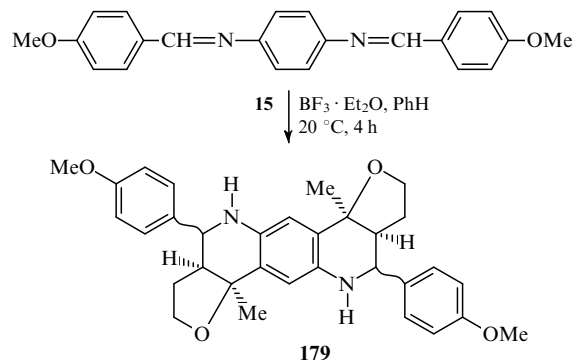
Acenaphthene derivatives **177a** and **177b** were obtained in an overall yield of 42%.



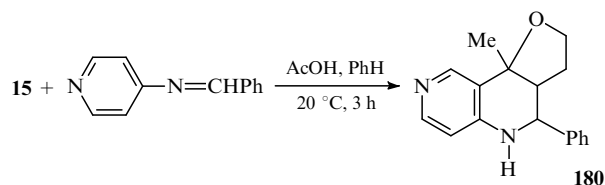
On heating with sulfur, the diastereomers **163** and **166** are converted into the quinoline derivative **178** in 70% yield.⁸³



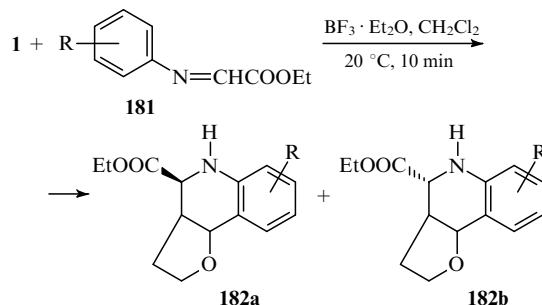
The reaction of *N,N'*-bis(*p*-methoxybenzylidene)-*p*-phenylenediamine with two moles of the enol ether **15** affords compound **179** in 32% yield.⁸³



Adduct **180** has been synthesised in 33% yield by the cycloaddition of the enol ether **15** to *N*-benzylidene-4-aminopyridine in the presence of acetic acid at ambient temperature.⁸⁵

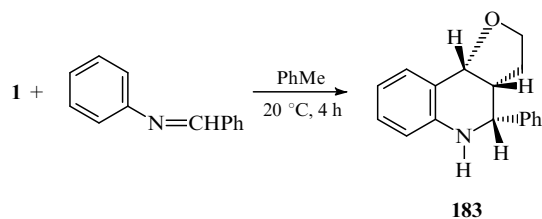


The stereochemistry of the reaction of the enol ether **1** with azomethines **181**, containing various substituents in the 4- or 2-positions of the benzene ring, has been studied.⁸⁶ The results obtained imply that this reaction proceeds non-stereoselectively, the isomers **182a** being usually formed in somewhat larger amounts than the isomers **182b**. The nature of the substituents R in the 4-position of the benzene ring exerts only a slight influence on the ratio between the diastereomers **182a** and **182b**, except for azomethines in which R = 4-OMe and R = 2-NO₂. In the latter case, only one isomer was obtained.



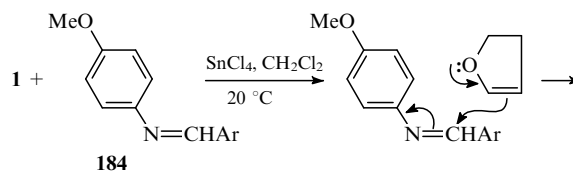
R	181	182	Yield (%)	
			182a	182b
H	H	H	31	23
4-Me	8-Me	8-Me	27	26
4-OMe	8-OMe	8-OMe	15	33
4-Cl	8-Cl	8-Cl	38	31
4-NO ₂	8-NO ₂	8-NO ₂	36	31
2-NO ₂	6-NO ₂	6-NO ₂	41	—

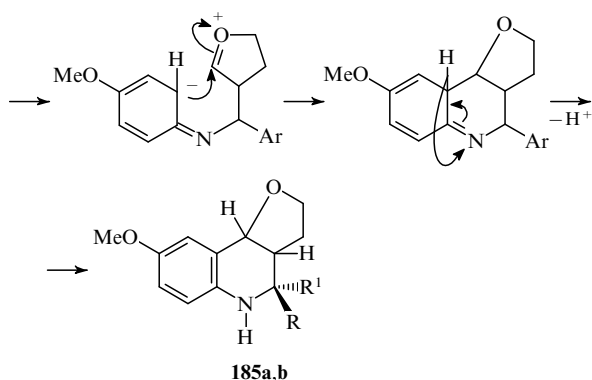
When various Lewis acids are used as catalysts in the reaction of the enol ether **1** with *N*-benzylideneaniline, the yields of the adducts **183** vary over a wide range.⁸⁷



Catalyst	EtAlCl ₂	ZnCl ₂	SnCl ₄	BF ₃ · Et ₂ O	AlCl ₃	TiCl ₄
Yield (%)	80	73.1	71.2	68.9	60.3	29.3

Japanese researchers⁸⁸ have studied the cycloaddition of the enol ether **1** to azomethines **184** in the presence of tin(IV) chloride and proposed a scheme for the formation of diastereomeric pairs of products **185**.

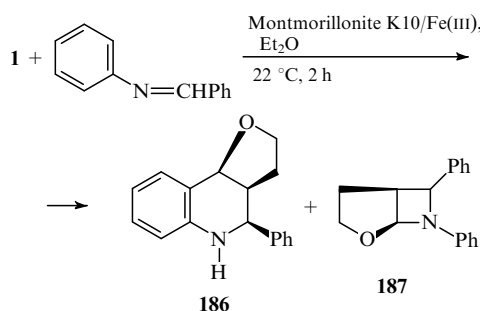




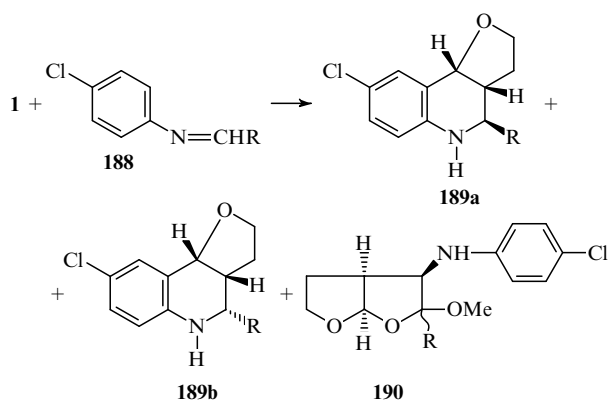
185a: R = H, R¹ = Ar; **185b:** R = Ar, R¹ = H.

Ar	Time /h	Yield (%)	
		185a	185b
2-Furyl	25.5	4.5	13
2-Thienyl	42.5	8.1	8.3
2-Pyridyl	48	17	—

The reaction of the enol ether **1** with *N*-benzylideneaniline in the presence of montmorillonite K10/Fe(III) occurs ambiguously: apart from the normal cycloaddition product **186** (yield 81%), the [2 + 2]-cycloaddition product, namely, 6,7-diphenyl-2-oxa-7-azabicyclo[3.2.0]heptane **187** is formed (yield 7%).⁸⁹

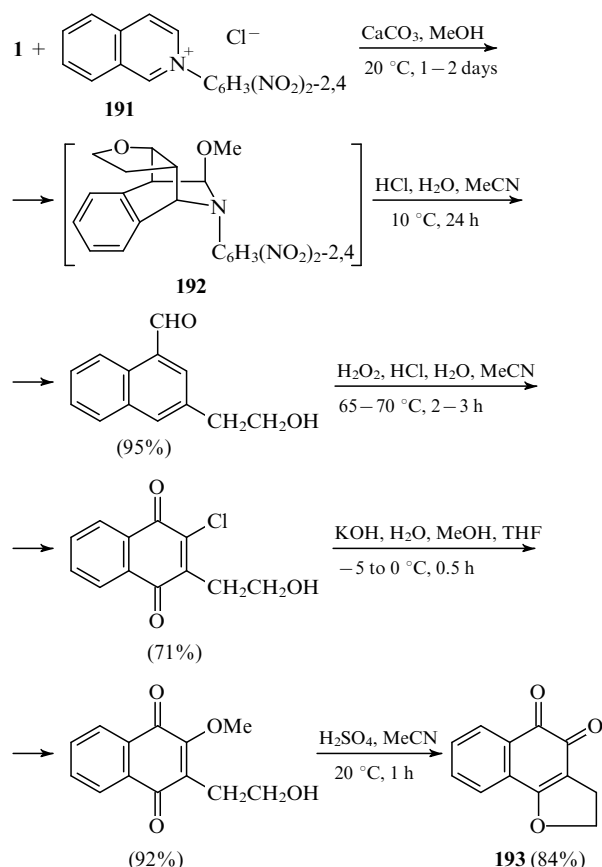


When the reaction of the compound **1** with azomethines **188** has been conducted in the presence of methanol and with Lewis acids as catalysts, together with the diastereomers **189a,b**, which are the normal reaction products, compounds **190** were obtained.⁹⁰

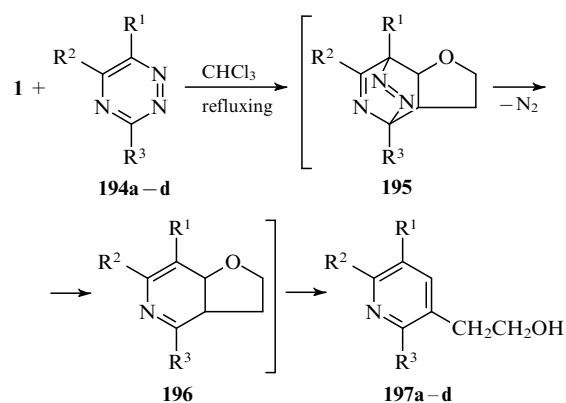


R = Ph, PhCO.

The reaction of isoquinolinium salt **191** and the enol ether **1** gave adduct **192**, which was converted into 4,5-dioxo-2,3,4,5-tetrahydronaphtho[1,2-*b*]furan **193** in four steps without isolation.⁹¹

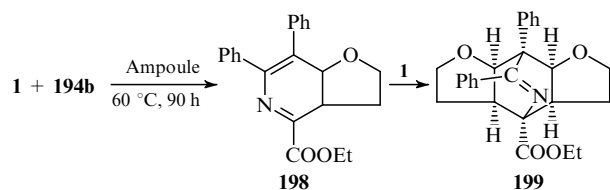


The interaction of the enol ether **1** with 1,2,4-triazine derivatives **194** begins with [4 + 2]-cycloaddition giving the corresponding adducts. Under reaction conditions (refluxing in chloroform), the adducts **195** formed in the first stage eliminate a nitrogen molecule and thus generate bicyclic compounds **196**, which then undergo cleavage of the five-membered ring and are converted into the pyridine derivatives **197**.⁹²

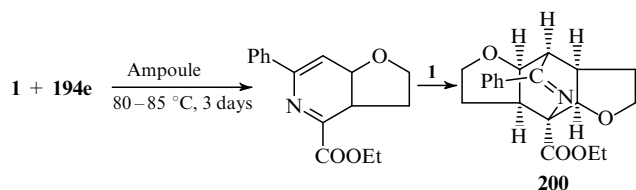


Compound	R ¹	R ³	Time /h	Yield (%)
197a	COOEt	COOEt	49	77
197b	Ph	COOEt	46	55
197c	COOEt	NHCOMe	120	67
197d	COOEt	Me	45	80

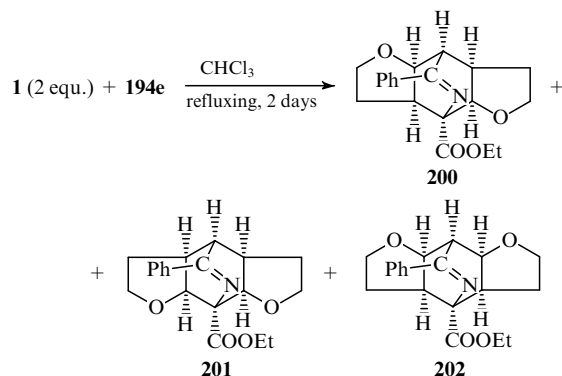
On heating in a sealed tube, the enol ether **1** reacts regioselectively with 1,2,4-triazine derivatives **194b** with the retention of the tetrahydrofuran ring to give compound **198**, which reacts regioselectively with another molecule of the enol ether **1** under the reaction conditions, and compound **199** is formed as the final reaction product (yield 69%).⁹²



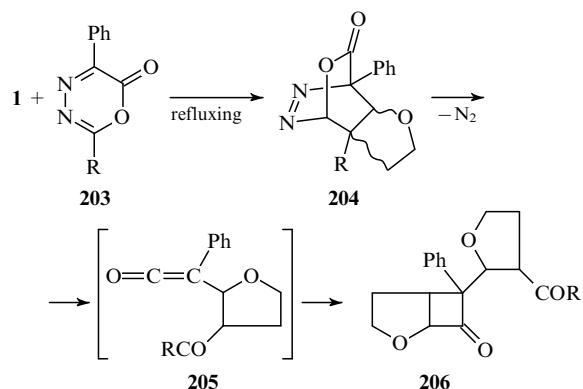
1,2,4-Triazine **194e** ($R^1 = \text{H}$, $R^2 = \text{Ph}$, $R^3 = \text{COOEt}$) also reacts with two molecules of the enol ether **1** when heated in a sealed tube; this reaction affords compound **200** in 68% yield. However, in this case, orientation of the first added molecule of the enol ether **1** is opposite.⁹²



It is of interest that the same reaction carried out in boiling chloroform affords all three possible regioisomers **200**, **201**, and **202** in 64%, 10%, and 10% yields, respectively.⁹²

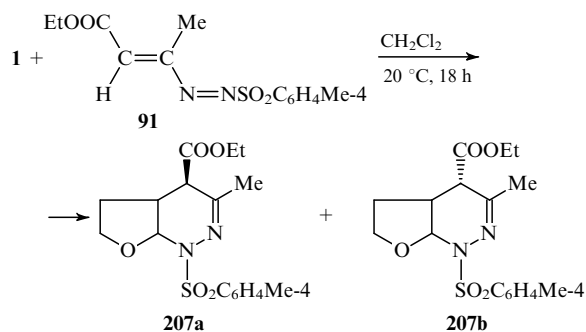


The adducts **204** obtained by heating the compound **1** with 1,3,4-oxadiazin-6-one derivatives **203** eliminate a nitrogen molecule under the reaction conditions, and the ketenes **205** thus generated react with a further molecule of the enol ether **1** giving finally bicyclo[3.2.0]heptan-6-one derivatives **206** as mixtures of diastereomers (yields 42% and 58%).⁹³

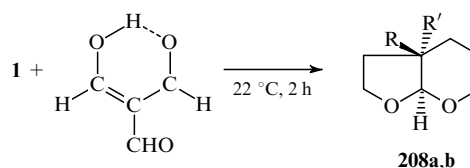


R = Ph, PhCH₂.

Ethyl *E*-3-(tolyl-*p*-sulfonylazo)but-2-enoate **91** reacts with 5-methyl-2,3-dihydrofuran **15** according to the [3 + 2]-cycloaddition reaction pattern.⁴⁹ However, the same heterodiene **91** reacts with 2,3-dihydrofuran also according to the [4 + 2]-cycloaddition scheme to give two diastereomers **207a,b**, one of which (**207b**) was isolated in a yield of 31%.⁴⁹



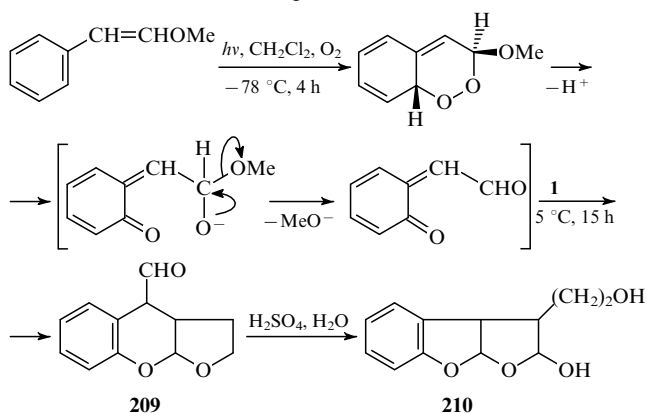
Trimethylmethane enters into the reaction with the enol ether **1** at 20 °C affording a mixture of isomeric 2,9-dioxabicyclo[4.3.0]non-3-ene derivatives **208a,b** (yield 73%, ratio **208a** : **208b** = 1 : 4).⁹⁴



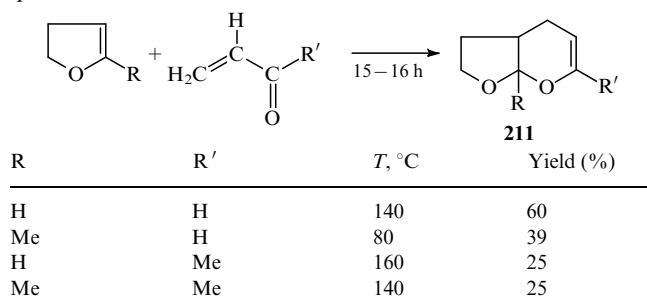
a: R = H, R' = OH

b: R = OH, R' = H

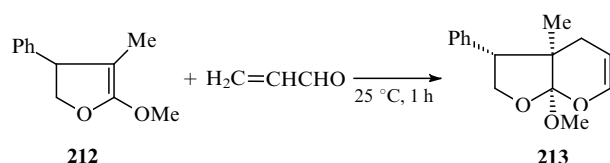
β-Methoxystyrene reacts with the enol ether **1** upon irradiation with the visible light in the presence of tetraphenylporphyrin to give aldehyde **209** (yield 13%), which is converted into the furobenzofuran derivative **210** on treatment with dilute sulfuric acid. Matsumoto and Kudora⁹⁵ proposed the following scheme for the formation of the compounds **209** and **210**:



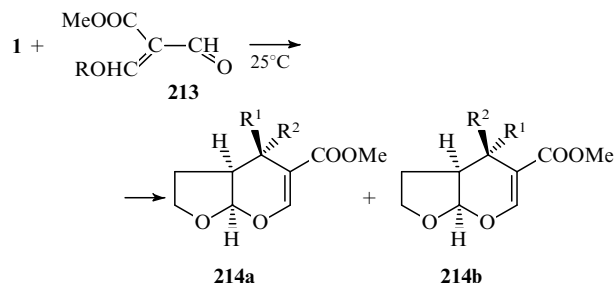
2,3,3a,7a-Tetrahydro-4*H*-furo[2.3-*b*]pyran and its derivatives **211** have been prepared by heating the enol ether **1** (or **15**) with acrolein or with methyl vinyl ketone in the presence of hydroquinone.⁹⁶



The [4 + 2]-cycloaddition of 5-methoxy-4-methyl-3-phenyl-2,3-dihydrofuran **212** to acrolein has been carried out⁹⁷ at 25 °C, which has led to the *cis*-isomer of 1α-methoxy-6α-methyl-7-phenyl-2,9-dioxabicyclo[4.3.0]non-3-ene **213**.

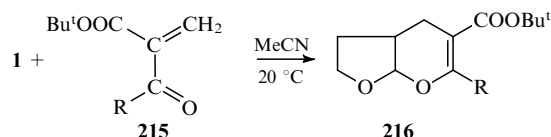


Diastereomeric compounds **214a,b** have been synthesised from the enol ether **1** and aldehydoesters at 25°C .⁹⁸



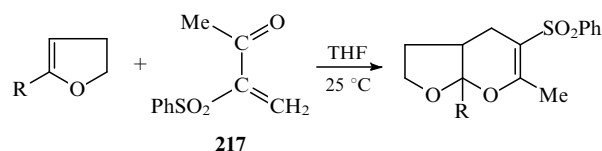
R	R ¹	R ²	Time /h	Yield (%)	Ratio 214a : 214b
H	H	OH	200	60	3 : 1
Ac	H	AcO	8–40	85	1 : 2
	H		40	86	1 : 2

α,β -Unsaturated ketones **215** containing the bulky COOBu^t group also react fairly readily with the enol ether **1** at 20°C giving adducts **216**.⁹⁹



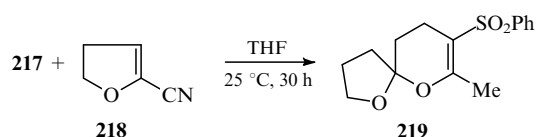
R	Et	PhCH ₂ CH ₂	C ₆ H ₁₁	Ph	4-BrC ₆ H ₄
Time /h	10	15	20	17	3
Yield (%)	40	36	54	70	79

The reaction of the enol ether **1** or 5-(1-hydroxy-1-methyl-ethyl)-2,3-dihydrofuran with 3-phenylsulfonylbut-3-en-2-one **217** has been reported.¹⁰⁰

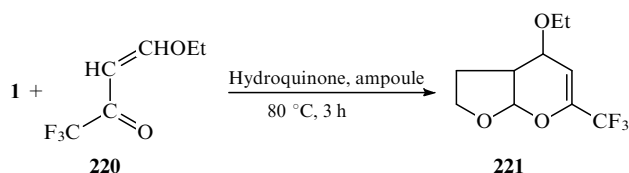


R	Time /h	Yield (%)
H	2.5	86
C(Me) ₂ OH	1	50

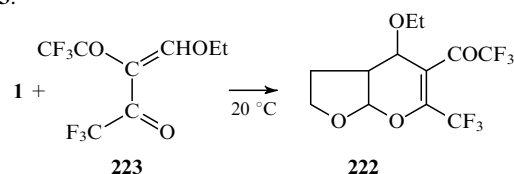
An unexpected result was obtained when the ketone **217** was made to react with 5-cyano-2,3-dihydrofuran **218**. Instead of a [4 + 2]-cycloaddition product, spiro-compound **219** was isolated in 35% yield.¹⁰⁰



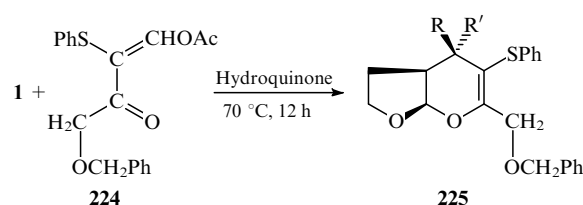
The reaction of 2,3-dihydrofuran **1** with 4-ethoxy-1,1,1-trifluorobut-3-en-2-one **220** occurs regioselectively but non-stereoselectively; this reaction leads to a mixture of diastereomers of 4-ethoxy-6-trifluoromethyl-2,3,3a,7a-tetrahydro-4H-furo[2,3-b]pyran **221** in 68% yield.¹⁰¹



The [4 + 2]-cycloaddition product **222** has been synthesised in 86% yield by the reaction of the compound **1** with heterodiene **223**.¹⁰²

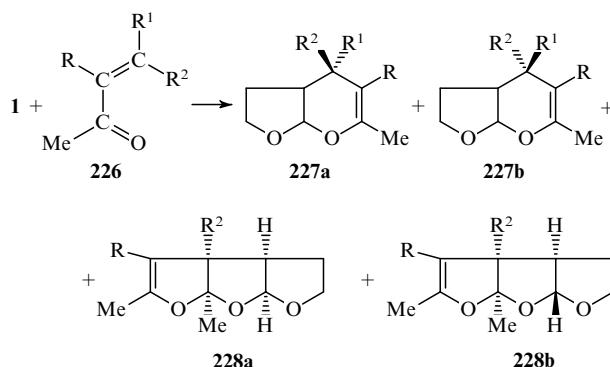


Heating of the enol ether **1** with heterodiene **224** has given compound **225** as a mixture of diastereomers.¹⁰³



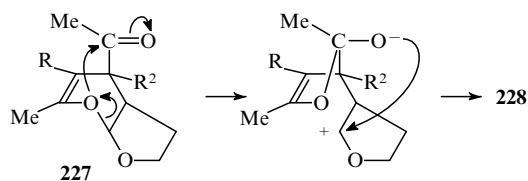
R	R'	Yield (%)
OAc	H	50
H	OAc	12.5

A more complex picture is observed when the enol ether **1** is introduced into the reaction with unsaturated ketones **226**. Depending on the nature of substituents in the ketone molecule, the process gives either adduct **227a** or a mixture of adducts **227a** and **227b** and compounds **228a** and **228b** resulting from their transformations.¹⁰⁴

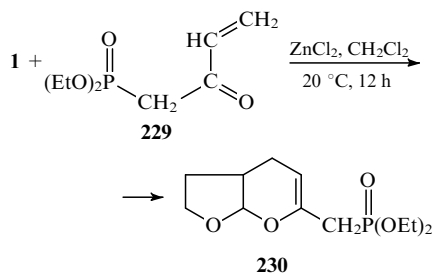


R	R ¹	R ²	T / °C	Time /h	Yield (%)
Ac	Ac	Ac	55	6	54 (227a) + 36 (228a)
H	H	Ac	85	29	90 (227a)
COOEt	Ac	COOEt	55	8	32 (227a) + 49 (227b) + 8 (228a) + 4 (228b)

The researchers cited¹⁰⁴ explained the formation of the compounds **228** from the adducts **227** in terms of the following scheme:

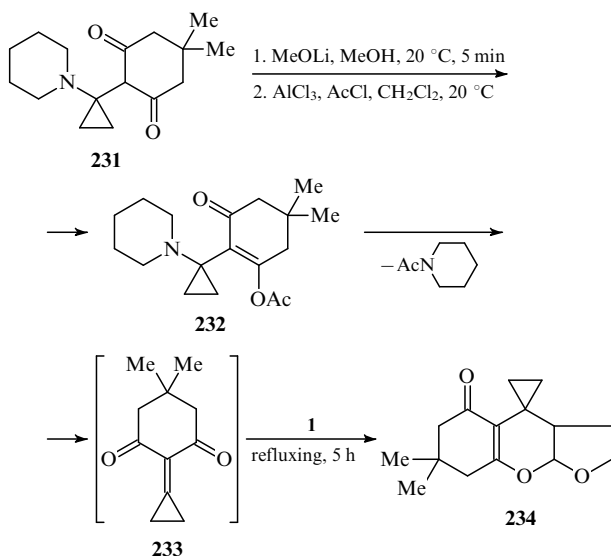


The reaction of the enol ether **1** with methyl vinyl ketone **229** in the presence of zinc chloride proceeds *endo*-selectively and gives rise to compound **230** (yield 89%).¹⁰⁵

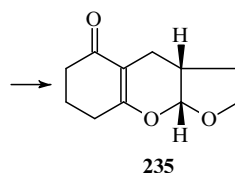
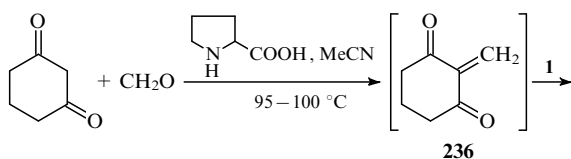


In the absence of zinc chloride, this reaction needs to be carried out in a sealed tube at 85 °C for 20 h.

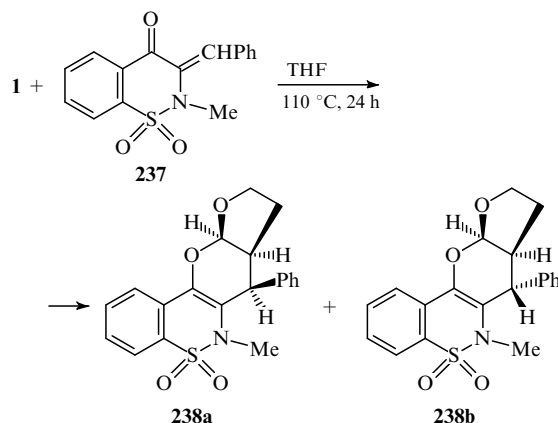
Treatment of diketone **231** with lithium methoxide and then by acetyl chloride affords the *O*-acetyl derivative **232**; on boiling in the enol ether **1**, this compound eliminates *N*-acetylpiperidine and is thus converted into a new diketone, compound **233**, which reacts with the enol ether **1** giving tricyclic compound **234** (yield 48%).¹⁰⁶



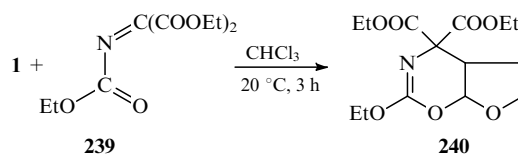
Compound **235** has been prepared by condensing the enol ether **1** with cyclohexane-1,3-dione and formaldehyde in the presence of proline. It is clear that the interaction of the diketone and formaldehyde results in the intermediate formation of heterodiene **236**, which undergoes [4+2]-cycloaddition to the enol ether.¹⁰⁷



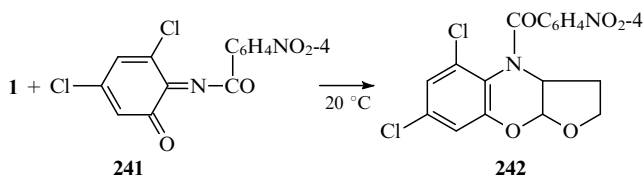
When heterodiene **237** is heated with the enol ether **1** in a sealed tube for a long period, two diastereomeric adducts **238a** and **238b** are produced (yields 60% and 10%).¹⁰⁸



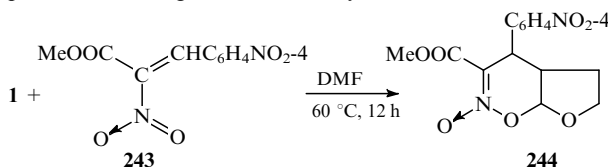
The [4+2]-cycloaddition of the enol ether **1** to compound **239** has led to adduct **240** (yield 61%).¹⁰⁹



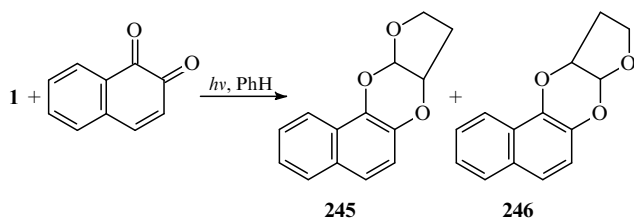
Of the two heterodiene systems, present in the compound **241**, C=N–C=O and N=C–C=O, the system that incorporates the carbon–oxygen semicyclic double bond is involved in the cycloaddition with the enol ether **1** affording adduct **242** in 90% yield.¹¹⁰



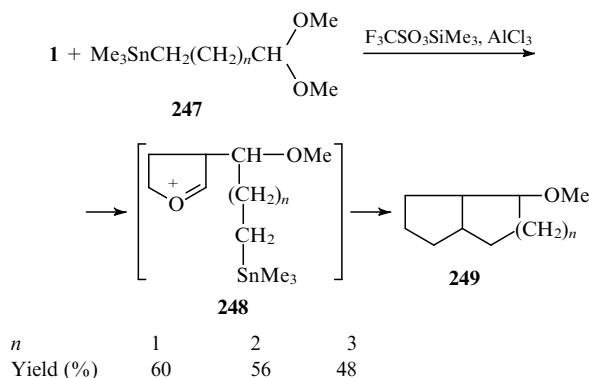
Nitroalkene **243** enters into Diels–Alder condensation with 2,3-dihydrofuran **1** on heating in DMF, the [4+2]-cycloaddition product **244** being formed in 80% yield.¹¹¹



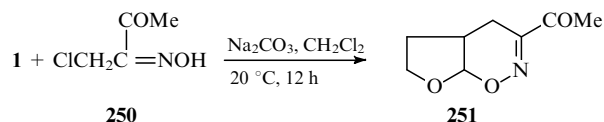
2,3-Dihydrofuran **1** and 1,2-naphthoquinone exposed to the radiation of a high-pressure mercury lamp ($\lambda = 340$ nm) interact following the [4+2]-cycloaddition pattern; this affords a mixture of two isomeric adducts **245** and **246**. A crucial influence on the yield of the adducts is exerted by the polarity of the solvent used. When the reaction is conducted in non-polar benzene ($D = 0.00$), the overall yield of the compounds **245** and **246** is 55%; in the case where acetonitrile ($D = 3.37$) is used, the overall yield of the adducts is only 4%.⁵²



The reaction of the compound **1** with dimethyl acetals **247** in the presence of trimethylsilyl trifluoromethanesulfonate and aluminium chloride involves the intermediate formation of the oxonium ions **248**, which are converted into the diastereomers of compound **249** under the reaction conditions.¹¹² This process can only formally be classified as cycloaddition.

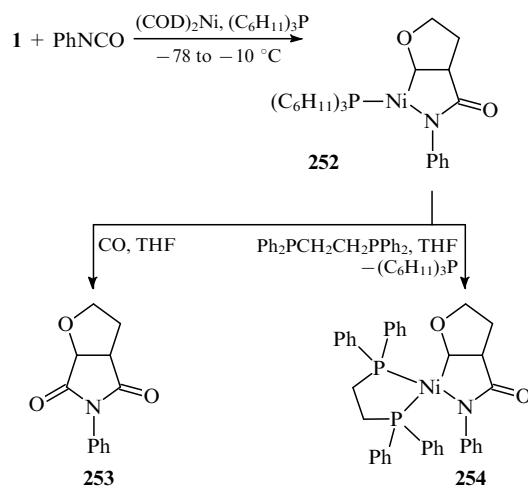


Similarly, 'formal cycloaddition' of the enol ether **1** to oxime **250** (treatment with sodium carbonate at room temperature) affords 3-acetyl-4*a*,5,6,7*a*-tetrahydro-4*H*-furo[3,2-*e*]-1,2-oxazine **251**.¹¹³

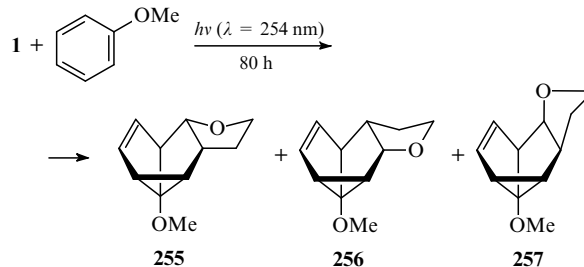


5. Other cycloaddition reactions

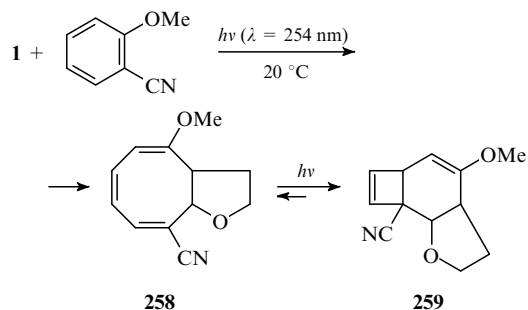
2,3-Dihydrofuran **1** has been made to react with phenyl isocyanate in the presence of bis(cyclooctadiene)nickel (COD)₂Ni and tricyclohexylphosphine at a low temperature; this gave organometallic compound **252** in 93.5% yield. The latter reacts with carbon monoxide or with 1,2-bis(diphenylphosphino)ethane resulting in the formation of furopyrrrole derivative **253** or organometallic compound **254** (yields 63.8% or 62%, respectively).¹¹⁴



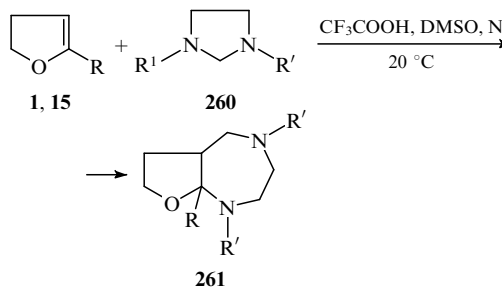
Three compounds: *exo*-isomer **255**, *exo*-isomer **256**, and *endo*-isomer **257**, have been isolated in 2 : 1 : 3 ratio from the products of the photochemical reaction of 2,3-dihydrofuran **1** with anisole.¹¹⁵



A totally different picture is observed in a photochemical reaction of 2,3-dihydrofuran **1** with the anisole derivative containing an electron-withdrawing cyano-group in the 2-position. The bicyclo[6.3.0]undecatriene derivative **258** is the primary reaction product, which isomerises upon irradiation into tricyclic compound **259**. An equilibrium shifted toward the compound **259** is established under the reaction conditions. The latter compound is converted into the bicyclic compound **258** on heating.¹¹⁶

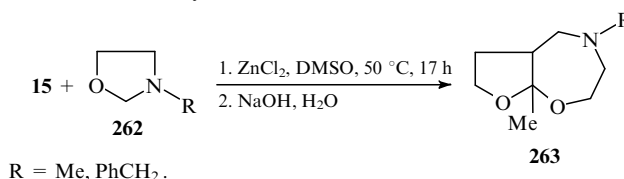


The reaction of 1,3-dialkylimidazolidines **260** with the enol ethers **1** or **15** in the presence of trifluoroacetic acid has led to octahydrofuro[3,2-*f*]-1,4-diazepine derivatives **261**.¹¹⁷



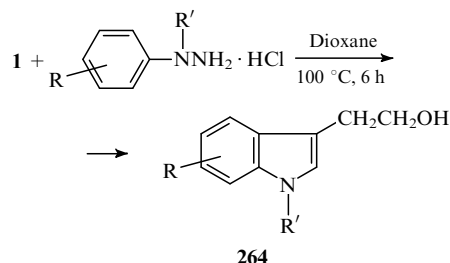
R	R'	Time /h	Yield (%)
H	Me	22	41
H	Bu	139	35
Me	Me	23	20

The reaction of 5-methyl-2,3-dihydrofuran **15** with 3-substituted oxazolidines **262** in the presence of Lewis acids is accompanied by expansion of the oxazolidine ring and results in the formation of 4-*R*-8*a*-methylperhydrofuro[3,2-*f*]-1,4-oxazepines **263** in 50% – 75% yields.^{118, 119}



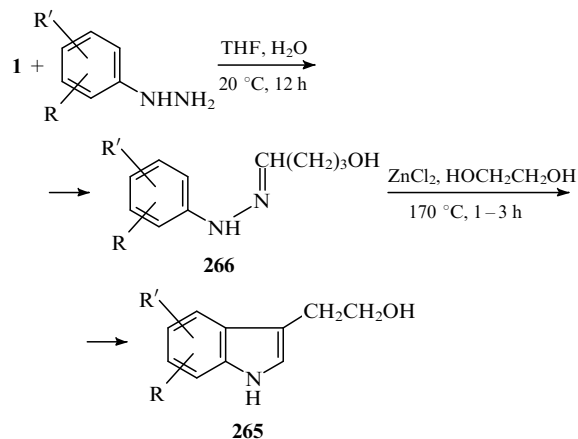
III. Recyclisation reactions

Two methods have been proposed for the synthesis of tryptophol derivatives **264**. The first method involves heating of a mixture of the enol ether **1** and arylhydrazine in dioxane for 6 h. The indole derivatives **264** are obtained without isolation of the intermediate hydrazones.^{120–122}



R	R'	Yield (%)	Ref.
H	H	30	55
5-Me	H	40	55
7-Me	H	20	55
7-MeO	H	25	55
H	Me	32	55
H	Ph	45	56
7-cyclo-C ₃ H ₅	H	25	56
7-Et	H	—	57

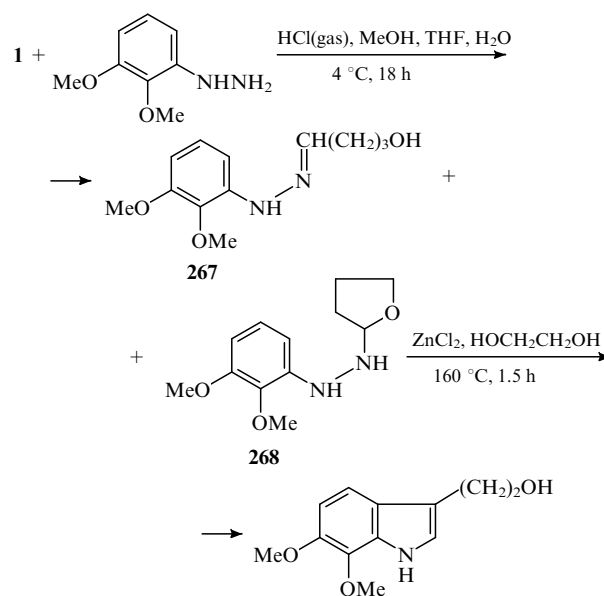
According to the second method, tryptophol derivatives **265** are prepared in two stages. Arylhydrazones **266** are obtained initially from the enol ether **1** and the corresponding arylhydrazines; then the arylhydrazones are cyclised by heating in the presence of zinc chloride under an inert atmosphere to give the target compounds **265**.^{123–125}



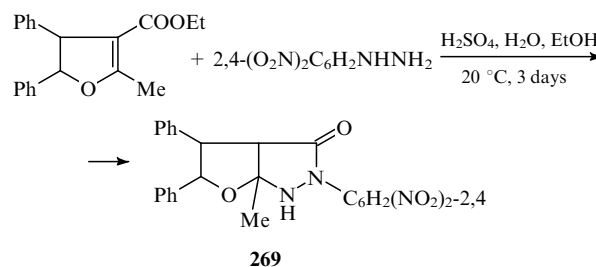
R	R'	Yield of 265 (%)	Ref.
H	7-I	48	123
6-F	7-I	—	124
6-F	7-Br	48	125

It has been shown¹²⁶ that the reaction of the compound **1** with 2,3-dimethoxyphenylhydrazine in the presence of hydrogen chloride at 4 °C affords two products, namely, arylhydrazone **267** (yield 42.5%) and the hydrazine derivative **268** (yield 42.5%).

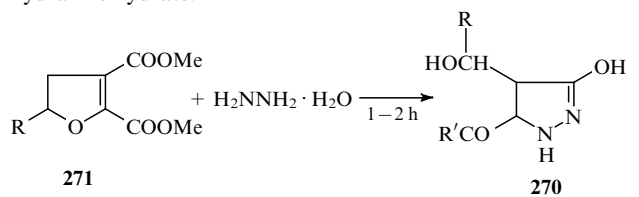
When the resulting mixture of **267** and **268** is heated under an inert atmosphere in the presence of zinc chloride, the compounds cyclise leading to only one product, 3-(2-hydroxyethyl)-6,7-dimethoxyindole, its yield being as low as 10%.¹²⁶



Cyclocondensation of ethyl 5-methyl-2,3-diphenyl-2,3-dihydrofuran-4-carboxylate with 2,4-dinitrophenylhydrazine in the presence of H₂SO₄ at 20 °C has led to 2-(2,4-dinitrophenyl)-6a-methyl-4,5-diphenyl-hexahydrofuro[2,3-*c*]pyrazol-3-one **269** in 18% yield.¹²⁷

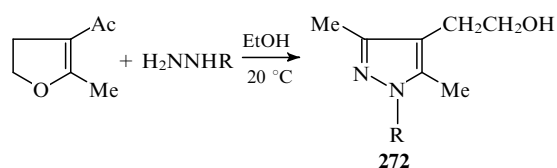


The pyrazole derivatives **270** have been prepared by recyclisation of 4,5-bis(methoxycarbonyl)-2,3-dihydrofurans **271** with hydrazine hydrate.¹²⁸



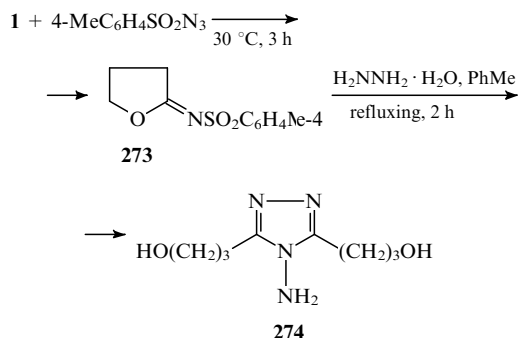
R	R'	Reaction conditions	Yield (%)
H	OMe	20 °C	59
H	NHNH ₂	boiling	90
Me	NHNH ₂	boiling	77
Et	NHNH ₂	boiling	87

The reaction of 4-acetyl-5-methyl-2,3-dihydrofuran with hydrazine, phenylhydrazine, or tosylhydrazine has led to compounds of the pyrazole series **272**.¹²⁹

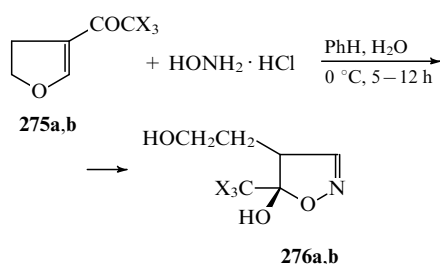


R	H	Ph	SO ₂ C ₆ H ₄ Me-4
Yield (%)	54	47	62

The reaction of the enol ether **1** with toluene-*p*-sulfonyl azide affords imine **273**, which is recycled to 4-amino-3,5-bis(3-hydroxypropyl)-1,2,4-triazole **274** (yield 88%) on heating with hydrazine hydrate in toluene.¹³⁰



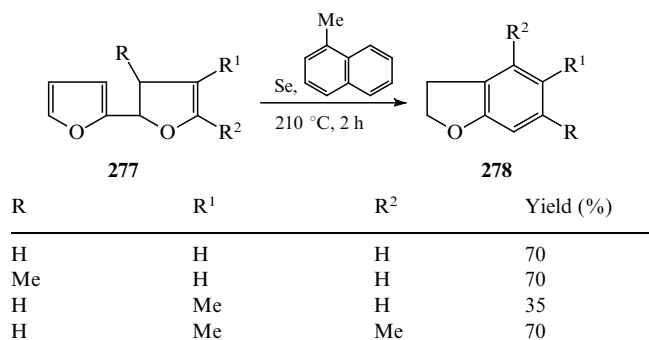
4-(Trihalomethylcarbonyl)-2,3-dihydrofurans **275** recycle on treatment with hydroxylamine in the presence of pyridine even at 0 °C to give 5-hydroxy-4-(2-hydroxyethyl)-5-trihalo-methyl-2-isoxazolines **276**.¹³¹



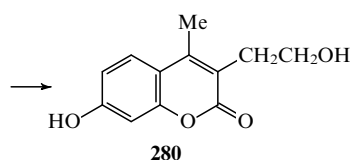
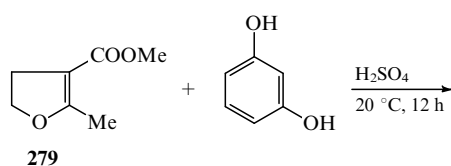
X = F (a), Cl (b).

The trifluoroacetyl derivative **275a** is more reactive. Its reaction is completed over a period of 5 h giving rise to compound **276a** in 90% yield. The compound **275b** reacts over a period of 12 h to give **276b** in 85% yield.¹³¹

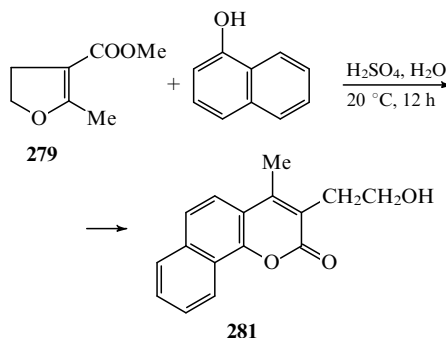
On heating with selenium in 1-methylnaphthalene, compounds **277** containing both furan and 2,3-dihydrofuran rings are converted into benzofuran derivatives **278**.¹³²



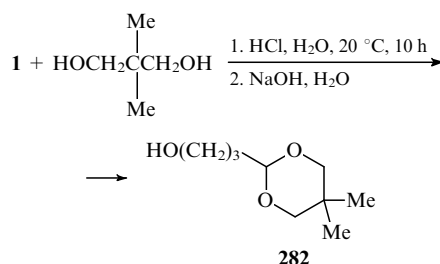
Condensation of methyl 5-methyl-2,3-dihydrofuran-4-carboxylate **279** with resorcinol in the presence of sulfuric acid gives 7-hydroxy-3-(2-hydroxyethyl)-4-methylcoumarin **280**.¹³³



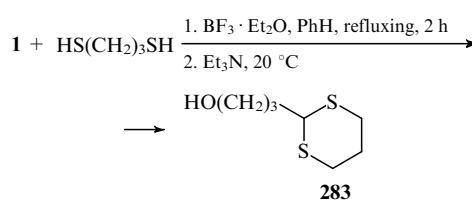
The 2,3-dihydrofuran **279** reacts with 1-naphthol in the presence of 80% sulfuric acid to afford the benzocoumarin derivative **281**.¹³³



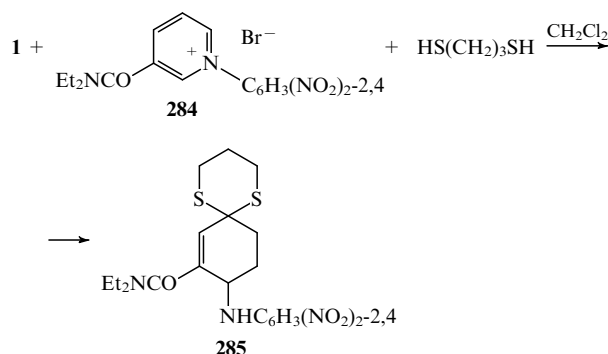
In the presence of hydrochloric acid, 2,3-dihydrofuran **1** reacts with 2,2-dimethylpropane-1,3-diol at room temperature, and the 1,3-dioxane derivative **282** is formed in 83% yield.¹³⁴



A sulfur-containing analogue of the compound **282** (compound **283**) has been synthesised in 43% yield by the reaction of the compound **1** with propane-1,3-dithiol in the presence of boron trifluoride etherate followed by treatment of the reaction product with triethylamine.¹³⁵

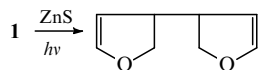


It has been reported¹³⁶ that the reaction of the salt **284** with 2,3-dihydrofuran **1** and propane-1,3-dithiol leads to compound **285**.



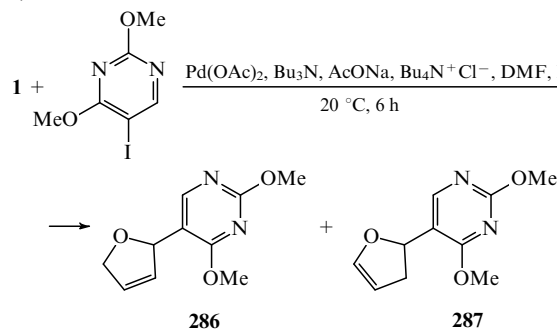
IV. Substitution of hydrogen atoms in 2,3-dihydrofurans

Photocatalytic heterogeneous dehydrodimerisation of the enol ether **1** in the presence of zinc sulfide and water results in the formation of bi(2,3-dihydrofuran-3-yl).¹³⁷

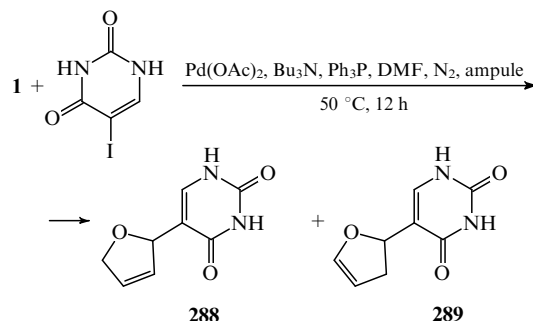


When 2,3-dihydrofuran **1** reacts with 5-iodo-2,4-dimethoxypyrimidine in the presence of palladium acetate, tributylamine, sodium acetate, and a phase transfer catalyst, the hydrogen atom in the 2-position of the enol ether is substituted, and the double bond in the dihydrofuran ring partly isomerises.

This gives two compounds **286** (yield 55%) and **287** (yield 26%).¹³⁸

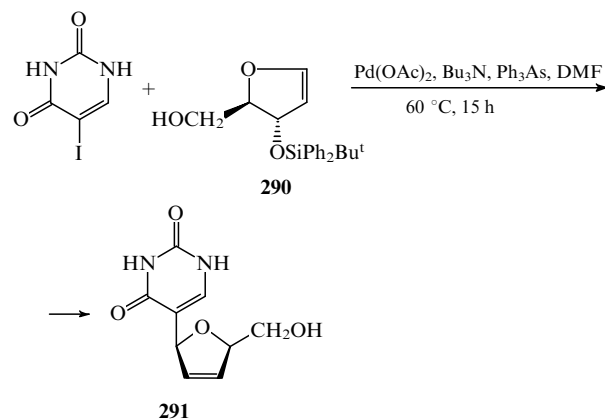


Two compounds **288** and **289** in an overall yield of 68% and in a ratio of 3 : 4 have also been synthesised by the reaction of the dihydrofuran **1** with 5-iodouracil in the presence of palladium acetate, tributylamine, and triphenylphosphine.¹³⁸

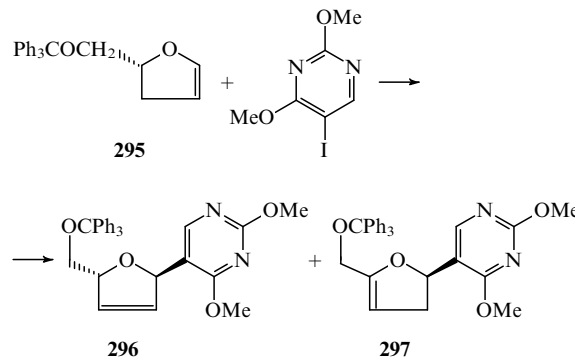


If triphenylarsine is used in this reaction instead of triphenylphosphine, the compounds **288** and **289** are formed over a period of 3 h at 50 °C in 58% overall yield and in a 2 : 3 ratio.¹³⁸

The reaction of 5-iodouracil with the 2,3-dihydrofuran derivative **290** in the presence of Pd(OAc)₂, Bu₃N, and Ph₃As under an inert atmosphere occurs stereoselectively and affords 5-(5-hydroxymethyl-2,5-dihydrofuran-2-yl)uracil **291** in 58% yield.¹³⁸

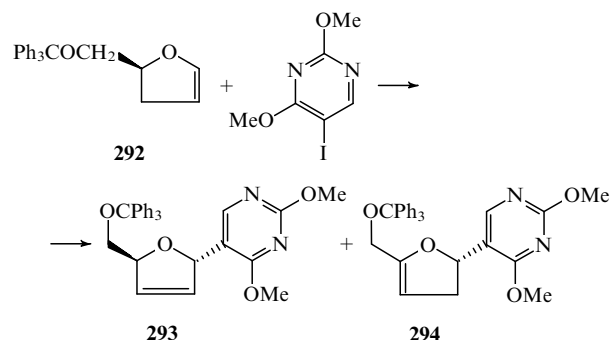


In order to prepare initial compounds for the synthesis of 2',3'-deoxy-*C*-nucleosides, the reaction of 5-iodo-2,4-dimethoxypyrimidine with 2(*R*)-(triphenylmethoxymethyl)-2,3-dihydrofuran **292** has been studied. By varying reaction conditions, Zhang and Daves¹³⁹ prepared compounds **293** and **294** in various proportions.



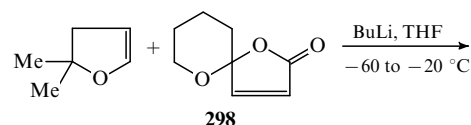
Reaction conditions	Yield (%)	
	293	294
Pd(OAc) ₂ , Et ₃ N, Bu ₄ N ⁺ Cl ⁻ ; H ₂ O, DMF, N ₂ , 20 °C, 20 h	56	31
Pd(OAc) ₂ , Ph ₃ As, Et ₃ N, MeCN, N ₂ , 75 °C, 10 h	18	59

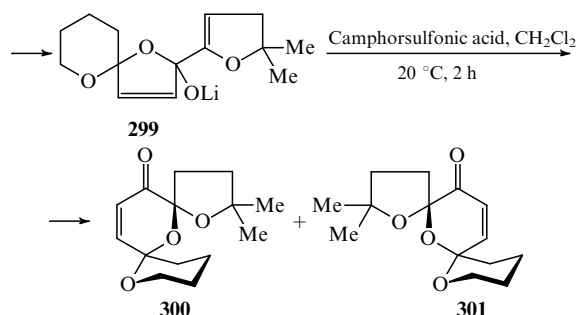
The reaction of 5-iodo-2,4-dimethoxypyrimidine with 2(*S*)-(triphenylmethoxymethyl)-2,3-dihydrofuran **295** also led to two isomers **296** and **297**, the ratio between them being dependent on the reaction conditions.¹³⁹



The reactions involving the compound **295** were carried out under the same conditions as those with the isomer **292**. The compounds **296** and **297** were obtained in the following yields: in water and DMF at 20 °C, 53% and 30%; in MeCN at 75 °C, 20% and 58%. When the reaction of the isomer **295** with the iodo-derivative was carried out in the presence of Pd(OAc)₂, Ph₃P, and Ag₂CO₃ in MeCN at 75 °C for 10 h under a nitrogen atmosphere, only the isomer **296** was formed in 40% yield.¹³⁹

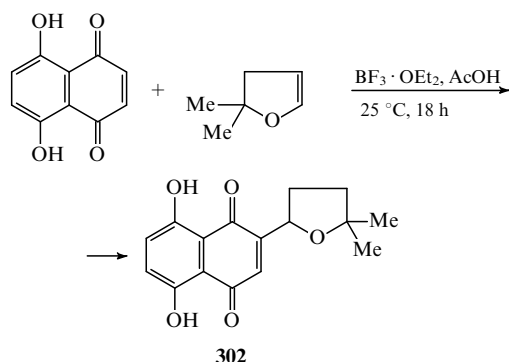
In the presence of butyllithium, 2,2-dimethyl-2,3-dihydrofuran reacts with 1,6-dioxaspiro[4.5]dec-3-en-2-one **298** to give the lithium derivative **299** arising due to the substitution of the hydrogen atom in the 5-position of 2,2-dimethyl-2,3-dihydrofuran. In the presence of camphorsulfonic acid, the lithium derivative **299** undergoes a rearrangement being thus converted into two compounds **300** and **301** (overall yield 15%, ratio 1 : 1).¹⁴⁰



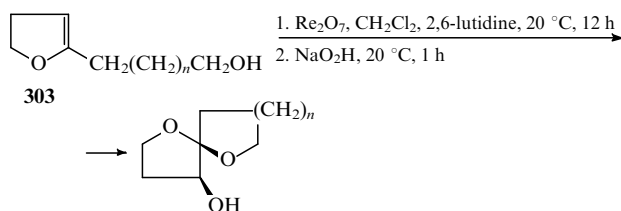


V. Addition to the double bond in 2,3-dihydrofurans

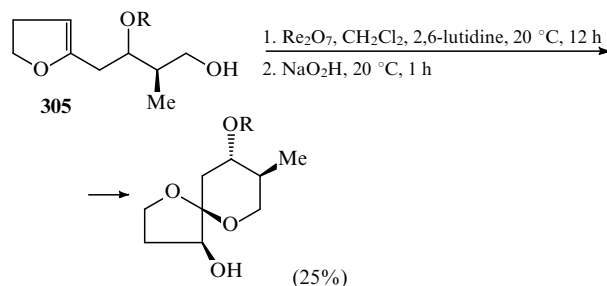
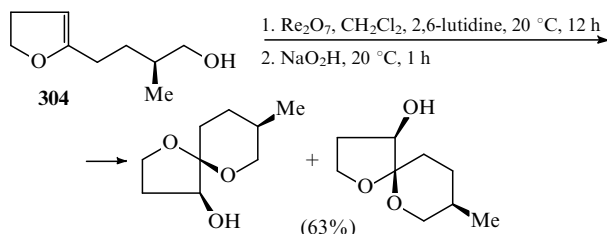
The addition product **302** has been synthesised in 40% yield by the reaction of 5,8-dihydroxy-1,4-naphthoquinone with 2,2-dimethyl-2,3-dihydrofuran in the presence of boron trifluoride etherate in acetic acid.¹⁴¹



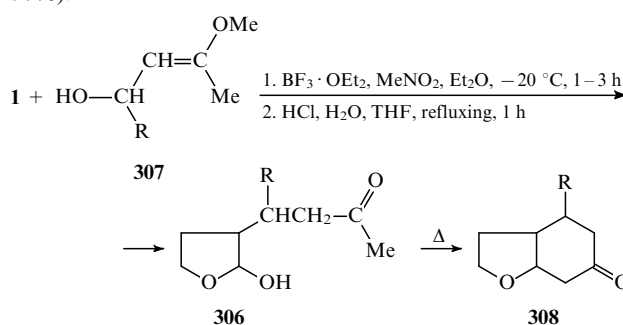
The 2,3-dihydrofuran derivatives **303–305** containing ω-hydroxyalkyl groups in the 5-position undergo spirocyclisation under the conditions of intramolecular addition–oxidation in the presence of Re₂O₇ under an inert atmosphere followed by treatment with sodium peroxide.



<i>n</i>	1	2
Yield (%)	18	48

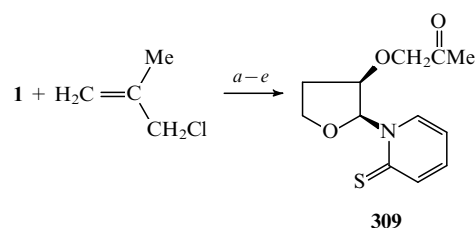


Ketones **306**, which are the addition products formed from the enol ether **1** and compounds **307**, are converted on heating into the perhydrobenzofuran-6-one derivatives **308** (yields 48%–50%).^{143, 144}



R = H, Me.

The tetrahydrofuran derivative **309** has been prepared from the enol ether **1**, 1-chloro-2-methylprop-2-ene, and di(2-pyridyl) disulfide (yield 6%).¹⁴⁵



a) 3-ClC₆H₄CO₂H; b) KH, THF, Bu₄N⁺I[−]; c) O₃, CH₂Cl₂, Ph₃P, −78 °C; d) H⁺, MeCN, H₂O; e) (2-C₅H₄NS)₂, Bu₃P, CH₂Cl₂, 0 to −20 °C, 1.5 h.

The reactions of 2,3-dihydrofuran **1** with uracil or its derivatives **310** containing various substituents in the 5-position have been studied in most detail. The influences of the substituents in the 5-position, of the catalysts and solvents used, and of the reaction temperature and time on the yields of the addition products have been studied. Table 2 presents the substituents R in the initial and final compounds, conditions under which the reactions were conducted, and the yields of the resulting compounds **311**.

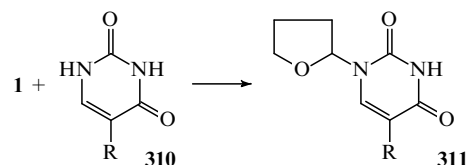
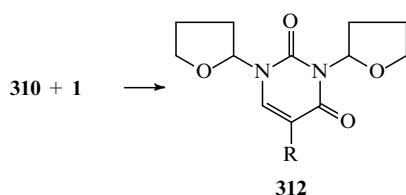


Table 2. Conditions of reactions^a of uracil derivatives **310** with 2,3-dihydrofuran **1** and yields of addition products **311**.

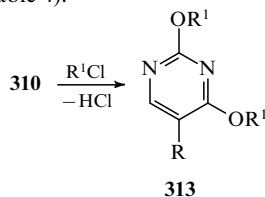
R	Reaction conditions	Yield (%)	Ref.
H	Py, 170 °C, 5 h	25	146
H	Py, 180 °C, 18 h	80	147
F	150–200 °C	82–88	148, 149
F	Py, THF, TiCl ₄	90	150
F	Py, 180 °C, 3 h	85	147
F	AlCl ₃ , DMF, CHCl ₃ , 60 °C, 12 h	70.2	151
F	MgCl ₂ , DMF, 120 °C, 3 h	71	152
F	Py, 4-MeC ₆ H ₄ SO ₃ H, 120 °C, 21 h	71	153
F	MeCOEt, 180 °C, 2 h	79	154
F	PdCl ₂ (PhCN) ₂ , MgCl ₂ , 18-crown-6, PhH, 80 °C, 7 h	54	155
F	PCl ₅ , (Me ₂ N) ₃ PO, 20 °C, 1 h	74.7	156
F	Et ₃ N·HCl, DMF, 100 °C, 8 h	65	157
F	AcOH, 90–95 °C, 5 h, dioxane	70	158
F	LiCl, 120 °C, 4 h	95	159
F	AlCl ₃ , Na ₂ CO ₃ , DMF, 130 °C, 4 h	60	160
F	DMF, 35 °C, 40 min	81.5	161
F	Py, F ₃ CCOOH, 60 °C, 6 h	73.9	162
F	AlCl ₃ , tris(3,6-dioxahexyl)amine, MeCN, refluxing, 2 h	80	163
F	1. Py, AcOH, 120 °C, 24 h; 2. AcONa, 70 °C, 4.5 h	45	164
F	Py, H ₂ O (ethanol), 185 °C, 3 h	73	165
F	SiCl ₄ , DMF, CH ₂ Cl ₂ , 20 °C, 5 h	82	166
Cl	Py, 150 °C, 6 h	85	147
Br	Py, 150 °C, 16 h	74	147
Me	Py, 180 °C, 8 h	90	147
COOMe	Py, 180 °C, 8 h	—	147
CN	Py, 150 °C, 6 h	65.7	147
I	Py, 170 °C, 5 h	—	146

^a At temperatures above 100 °C, the reactions were carried out in an autoclave.

Under certain conditions, the reactions of the uracil derivatives **310** with excess enol ether **1** have led to the corresponding 1,3-di(tetrahydrofuran-2-yl)uracil derivatives **312** (Table 3).



Yet another approach to the synthesis of the compounds **311** and **312** has been developed. According to this approach, 2,3-dihydrofurans **1** and bis-ethers **313**, prepared from the corresponding uracil derivatives **310**, are used as the initial compounds (Table 4).



R¹ = CMe₃, SiR₃², SnR₃² (R² = Alk).

The reaction of equimolar amounts of the dihydrofuran **1** and the compound **310** with Me₂SiCl₂ in DMF and CH₂Cl₂ at 20 °C for 6 h gives adduct **311** (R = F) in 84% yield. If the compounds **310** and **1** in a ratio of 1 : 2 react at 20 °C for 30 h, the reaction leads to a mixture of the compounds **311** (R = F) and **312**

Table 3. Conditions of reactions of uracil derivatives **310** with 2,3-dihydrofuran **1** and yields of compounds **312**.

R	Reaction conditions	Yield (%)	Ref.
H	Py, 180 °C, 20 h	82.1	147
F	LiCl, Cl ₂ CHCHCl ₂ , refluxing, 4.5 h	78.4	167
F	DMF, 135 °C, 20 h	42	168
F	AlCl ₃ , Py, 130 °C, 3 h	70	169
F	Py, 160 °C, 18 h	90	147
F	150 °C, 6 h	65	170
F	SiCl ₄ , DMF, CH ₂ Cl ₂ , 20 °C, 5 h	75	171
Cl	Py, 150 °C, 15 h	86.6	147
Br	Py, 150 °C, 15 h	86.8	147
Me	Py, 180 °C, 15 h	91.9	147
CONH ₂	Py, 150 °C, 15 h	93.2	147
COOMe	Py, 140 °C, 6 h	11	147

^a Excess 2,3-dihydrofuran was used.

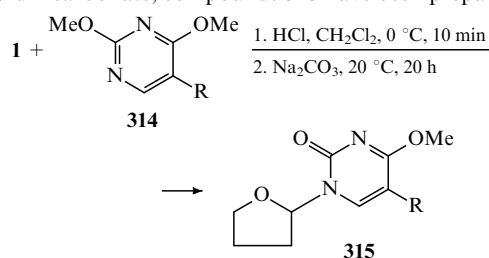
Table 4. Conditions of reactions of bis-ethers **313** with 2,3-dihydrofuran **1** and yields of compounds **311**.

R	R ¹	Reaction conditions	Yield (%)	Ref.
F	SiMe ₃	4-MeC ₆ H ₄ SO ₃ H, CH ₂ Cl ₂ , refluxing, 4 h	86.2	172
F	SiMe ₃	AlCl ₃ , LiI, I ₂ , H ₂ O, 70 °C, 3.5 h	80	171
F	SiMe ₃	SnCl ₄ , CH ₂ Cl ₂ , refluxing 3 h	79.4	173
F	SiMe ₃	SO ₂ Cl ₂ , THF, 20 °C, 15 h	50	174
F	SiMe ₃	2,4-lutidine, CH ₂ Cl ₂ , refluxing, 2 h	92.3	175
F	SiMe ₃	PyH·HCl, MeCN, 20 °C, 5 h	89.6 ^a	176
F	SiMe ₃	SnCl ₄	90	177
F	SiMe ₃	Amberlite IR-120, CH ₂ Cl ₂ , refluxing, 6 h	83	178
F	SiMe ₃	H ₃ BO ₃ , AlCl ₃ , PyH, refluxing, 1 h	65	179
F	SiMe ₃	4-MeC ₆ H ₄ SO ₃ H, MeCN, 130 °C, 40 min	71	180
F	SiMe ₃	HCl, CH ₂ Cl ₂ , EtOH, 0 °C, 0.5 h	80	181
F	CMe ₃	PyH·HCl, PyH, refluxing, 3 h	65	182
F	SnMe ₃	AlCl ₃ , MeCN, H ₂ O, 60 °C, 3 h	70	183
Br	SiMe ₃	HCl, CH ₂ Cl ₂ , EtOH, 0 °C, 0.5 h	75	181
I	SiMe ₃	NaI, CH ₂ Cl ₂ , refluxing, 3.5 h	79.6	184
Me	SiMe ₃	HCl, CH ₂ Cl ₂ , EtOH, 0 °C, 0.5 h	70	181
COMe	SiMe ₃	Na ₂ CO ₃ , CH ₂ Cl ₂ , 20 °C, 18 h	66	185

^a Compound **312**.

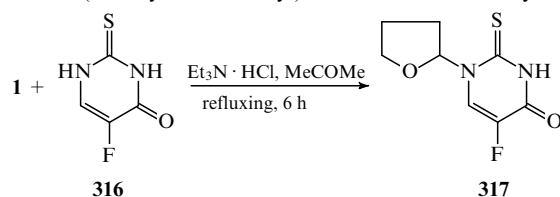
(R = F), their yields being 40% and 41%, respectively.¹⁸⁶ The interaction of 5-fluorouracil with the compound **1** and Me₂SiCl₂ in the presence of triethylamine in CH₂Cl₂ at 20 °C for 6 h affords the compound **311** (R = F) in 98% yield.¹⁸⁷

By successive treatment of a mixture of dimethoxy-derivatives **314** and the dihydrofuran **1** with hydrogen chloride and with sodium carbonate, compounds **315** have been prepared.¹⁸⁸

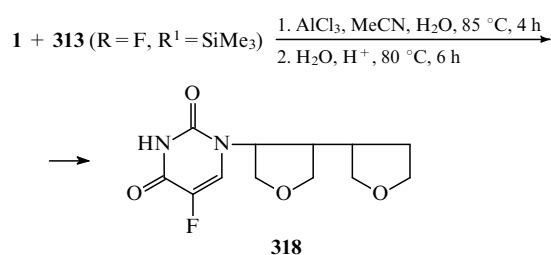


R H Me Br I
Yield (%) 86 40 31 33

5-Fluorothiouracil **316** adds to the compound **1** in the presence of triethylamine hydrochloride in boiling acetone giving 5-fluoro-1-(tetrahydrofuran-2-yl)thiouracil **317** in 65% yield.¹⁸⁹

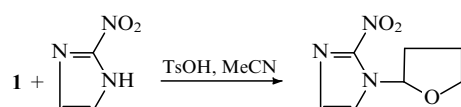


A method for the synthesis of 3-[4-(5-fluorouracil-1-yl)tetrahydrofuran-3-yl]tetrahydrofuran **318** (yield 16%) has been patented.¹⁹⁰ The method involves the reaction of the dihydrofuran **1** with the bis-ether **313** ($\text{R} = \text{F}$, $\text{R}^1 = \text{SiMe}_3$) in the presence of aluminium chloride followed by treatment of the reaction product with water at pH 4.¹⁹⁰

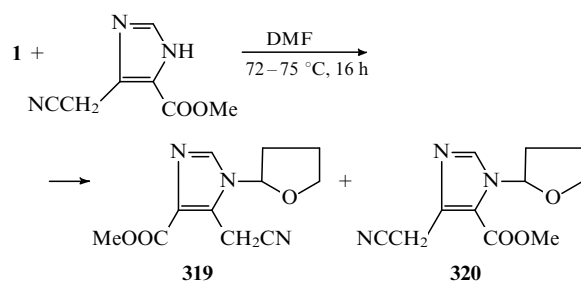


2-Morpholinotetrahydrofuran has been obtained by the addition of morpholine to the compound **1** in the presence of the $\text{Pd}(\text{SCN})_2/\text{P}(\text{OPh})_3$ catalyst at 20 °C for 15 h.¹⁹¹

2-Nitroimidazole adds to the compound **1** in the presence of toluene-*p*-sulfonic acid.¹⁹²



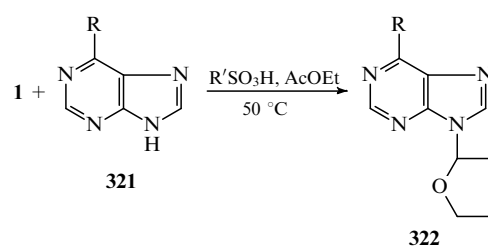
The addition of methyl 5-cyanomethylimidazole-4-carboxylate di(*p*-nitrophenyl) phosphate to 2,3-dihydrofuran **1** on heating in an autoclave occurs non-regioselectively and gives two compounds **319** and **320** (yields 50% and 20%).¹⁹³



2-(1,2,4-Triazol-1-yl)tetrahydrofuran has been prepared in 90% yield by the reaction of the dihydrofuran **1** with 1,2,4-triazole in the presence of 4- $\text{MeC}_6\text{H}_4\text{SO}_3\text{H}$ in DMF.¹⁹⁴

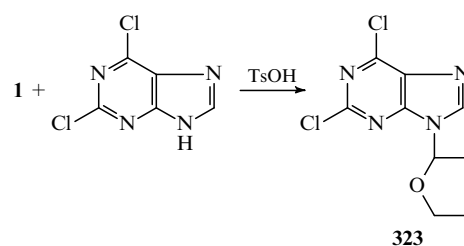
2-(Benzotriazol-1-yl)tetrahydrofuran has been obtained in a quantitative yield by refluxing the compound **1** with benzotriazole in tetrachloromethane for 5 h.¹⁹⁵

Purine derivatives **321** containing substituents in the 6-position have been made to react with dihydrofuran **1** in the presence of organic sulfonic acids; this reaction afforded addition products **322**.¹⁹⁶⁻¹⁹⁸

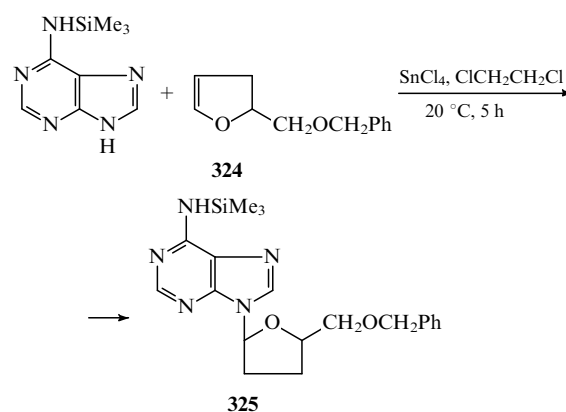


R	R'	Time /h	Yield (%)	Ref.
	4-MeC ₆ H ₄	24	86	196
	4-MeC ₆ H ₄	12	71.4	197
	Et	12	31	198
	Et	12	28	198

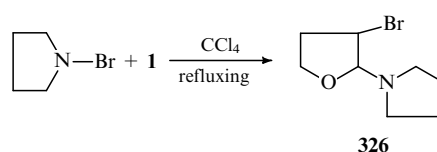
2,6-Dichloropurine adds to the dihydrofuran **1** in the presence of toluene-*p*-sulfonic acid to give 2,6-dichloro-9-(tetrahydrofuran-2-yl)-9*H*-purine **323** in 88% yield.¹⁹⁹



By the reaction of 2-benzyloxymethyl-2,3-dihydrofuran **324** with 6-(trimethylsilylamino)purine at ambient temperature in the presence of tin(IV) chloride, compound **325** has been synthesised in 53% yield.²⁰⁰

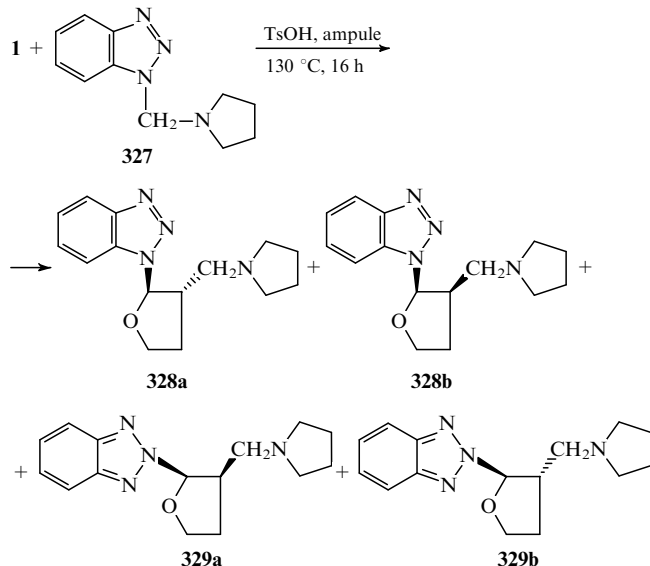


Refluxing of the compound **1** with 1-bromopyrrolidine in tetrachloromethane leads to 3-bromo-2-pyrrolidinotetrahydrofuran **326** in 29% yield.²⁰¹

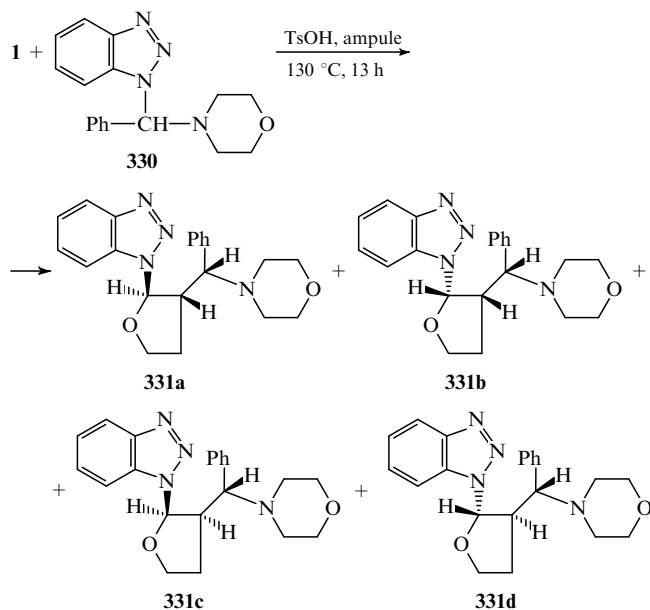


A fairly complex picture has been observed when 2,3-dihydrofuran **1** has been introduced in the reaction with 1-substituted benzotriazole derivatives.

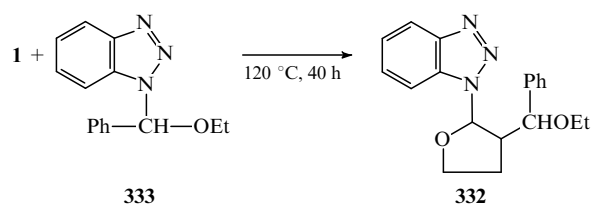
When the enol ether **1** is heated with 1-pyrrolidinomethylbenzotriazole **327** in the presence of toluene-*p*-sulfonic acid in a sealed tube, a mixture of two pairs of diastereomers **328a,b** (yields 19% and 24%) and **329a,b** (yields 3% and 53%) is formed.²⁰²



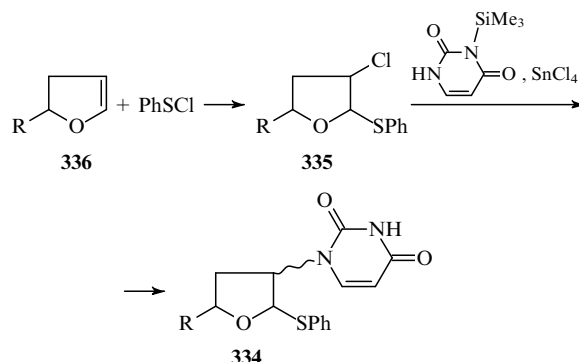
The reaction of 2,3-dihydrofuran **1** with benzotriazole derivatives **230** under the same conditions gives rise to the normal addition product as a mixture of four isomers (2*R*, 3*S*, 6*R*)-**331a**, (2*S*, 3*S*, 6*R*)-**331b**, (2*R*, 3*R*, 6*R*)-**331c**, and (2*S*, 3*R*, 6*R*)-**331d**.²⁰²



A mixture of four isomers of compound **332** has been obtained by heating the dihydrofuran **1** with 1-(α -ethoxybenzyl)benzotriazole **333** in a sealed tube.²⁰³

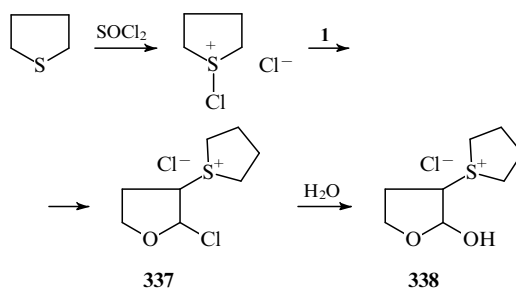


Tetrahydrofuran derivatives **334**, containing an uracil residue in the 4-position, have been synthesised by treating the adducts **335**, prepared by the addition of phenylsulfonyl chloride to dihydrofurans **336**, with *N*-trimethylsilyluracil in the presence of tin(IV) chloride.²⁰⁴

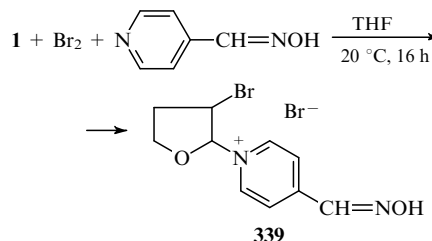


R = H, CH₂OSiPh₂Bu^t.

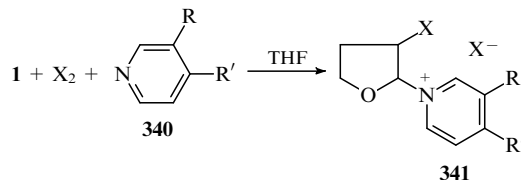
The reaction of 2,3-dihydrofuran with tetrahydrothiophene and thionyl chloride in sulfur dioxide has led to salt **337**, which was converted into the chloride of the hydroxy-derivative **338** through the action of water; the compound **338** was characterized as the corresponding picrylsulfonate (yield 19.5%).²⁰⁵



4-Formylpyridine oxime reacts with the compound **1** and bromine in THF to give the pyridinium salt **339** (yield 74%).²⁰⁶



A similar interaction of pyridine derivatives **340** with halogens and the dihydrofuran **1** resulted in the formation of salts **341**.²⁰⁶



X	R	R'
Cl	H	H
Br	CH=NOH	H
I	Me	H

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^c — Chem. Heterocycl. Compd. (Engl. Transl.)

Intermolecular interaction in polymers and the physical network model

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Abstract. The current views on the nature of the intermolecular interaction and the interchain organisation of polymers in the rubber-elastic state are described. The possibility of representing the system of intermolecular interactions by an infinite network of physical links (the physical network model) is considered. Polymeric physical networks are compared with associated species formed in low-molecular-mass organic compounds containing localised intermolecular interaction centres. The principal physical properties of polymers are analysed on the basis of the physical network model. The bibliography includes 280 references.

I. Introduction

The science of the structures of amorphous polymers has a long history. The fundamental ideas about the nature of the elasticity of elastomeric networks, introduced in the 1930s by Mark, Guth and Kuhn¹ and based on the model of overlapping statistical coils,^{2–4} made it possible to account for many thermodynamic and mechanical properties of elastomers. In the 1960s an attempt was made to re-examine the existing ideas about the structures of amorphous polymers on the basis of Frenkel's concept⁵ of the existence of a quasi-crystalline short-range order in liquids. Kargin, Kitaigorodskii, and Sloninskii put forward the hypothesis of the 'packet' structure of amorphous polymers.⁶ According to this model, the principal structural element of this system is not the macromolecule proper but an intermolecular packet consisting of several macromolecules in the uncoiled conformation arranged in parallel.^{7–9} However, the packet model encountered extremely serious objections. Flory² demonstrated theoretically that the volume effects in the polymer vanish with increase in the concentration of the solution and that the macromolecule in a block has the form of an unperturbed statistical coil. Calculations by the Monte Carlo method yield the same result:^{10–12} modelling of the conformations of nonintersecting chains showed that the gradual filling of a limited volume makes it possible to attain a

packing density of the segments which corresponds to the density of the block polymer with retention of the Gaussian coil conformation. Conformational analysis of macromolecules on the basis of the rotational-isomeric model^{3,4,13} also led to the conclusion that the macromolecule, having a Gibbs free energy minimum, should contain a fairly large number of bonds in the gauche-position. Convincing evidence in support of the amorphous polymer model, consisting of self-intersecting random coils, was obtained with the aid of the small angle neutron scattering technique.¹⁴ Direct measurement of the neutron diffraction in deuterated specimens of vitreous polystyrene^{15–17} and poly(methyl methacrylate)¹⁸ and also in a polyethylene melt^{18–20} showed that the mean square dimensions of the macromolecules in a block and in dilute ideal solutions are the same within the limits of ~10%.

All this led not only to the complete rejection of the 'packet' model but also to the denial by many investigators of the very possibility of the formation of any kind of structures in amorphous polymers. This conclusion cannot of course fail to give rise to objections. The set of accumulated experimental data shows that an ideal polymer, having the form of a structureless liquid consisting of self-intersecting random coils, is an exception rather than the rule. Indeed, the mechanical behaviour of network elastomers corresponding to this model occurs only under special conditions: when they are in a swollen state or for extremely small elongations.²¹ In other cases, deviations from the predictions of the theory of rubber elasticity are observed. This is evidently associated not only with the imperfection of the theory itself^{22–25} but also with the lack of correspondence between the structures of real networks and the structureless polymer model.^{26–28}

It is essential to mention the structural inhomogeneity of polymers at the molecular (compositional),²⁹ topological, and supermolecular (inhomogeneity arising from fluctuations and morphological and microphase formations) levels. One should also bear in mind that the range of polymers employed in practice is extremely wide and includes systems such as thermoreversible gels, block copolymers, interpenetrating polymer networks, and polyelectrolytes.

In the present review, an attempt is made to describe the current ideas concerning the structures of polymer systems in the rubber-elastic state and to analyse on the basis of the physical network model the principal physical properties of polymers of this kind.

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II. Intermolecular interaction in a 'structureless' polymer system

First of all, we shall consider the structureless model of the structure of a polymeric body in which the only factor taken into account is the presence of long chains and the only form of intermolecular interaction (IMI) is repulsion due to their mutual impermeability.

1. The topological network model (entanglements network)

The simplest and at the same time the most evident feature of a 'structureless' system is the topological limitations induced by the fact that the chains cannot intersect. As early as 1944, it was observed that the modulus of elasticity of vulcanised butyl rubber differs from the values calculated on the basis of the kinetic theory of rubber elasticity.³⁰ This was attributed to the presence of three kinds of network defects: ends, loops, and entanglements. The latter exist in the network before cross-linking, cross-linking merely leading to their fixation and imparting to them the ability to be manifested as additional nodes.

The first studies on natural rubber already revealed the reversibility of its deformations, which is manifested when the period during which the specimen is maintained under load is fairly short.³¹ This effect was explained by the intertwining of the molecules with formation of entanglements, which in the course of a short time act similarly to chemical cross-links. Later several characteristic features of the mechanical behaviour of polymers, caused by the interchain interaction, were observed. These include the characteristic inflection in the plots of the viscosity of polymer melts and solutions against their molecular mass and concentration, the existence on the thermomechanical curves of a plateau corresponding to the quasi-equilibrium rubber-elastic state, and the presence of a long-time region on relaxation time spectra. The terms 'entanglements' (coupling), 'temporary cross-linking' and 'physical network' are employed in the literature for the description of these phenomena.

The first systematic studies on the physical network in elastomers were carried out by Tobolsky.^{31–33} As early as 1946, a model was proposed for a network elastomer, according to which the nodes may be disrupted by thermal fluctuations and then reformed.³¹ In this case, there is a possibility of a characteristic viscoelastic behaviour of the elastomer: an elastic response on rapid application of a load and viscous flow and relaxation of stress on slow application of a load. An attempt has been made in a monograph³³ to arrange systematically the viscoelastic properties associated with the appearance of an entanglements network and to estimate the length of the chains between the entanglements on the basis of the theory of rubber elasticity.

Several reviews have been devoted to the problem of entanglements as a specific form of intermolecular interaction in polymers.^{34–37}

Although the existence of chain entanglements appears entirely evident, no one has succeeded in observing them directly. The deviation of the real elastic properties of an elastomer from those predicted by the classical theory of rubber elasticity is usually regarded as evidence for topological limitations. However, the existence of topological limitations does not yet imply that the entanglements are indeed in regions where the chains are entangled and intertwined. In this connection, several theoretical attempts were made to estimate the probability of the formation of an entanglement on the basis of the geometrical chain parameters. Thus Hoffmann³⁸ attempted to estimate the molecular mass of the chain section between entanglements. He suggested that the entanglements represent the type of intermolecular contacts in which one chain forms a loop around another. The calculation was performed for a polymethylene chain subject to the condition that the loops are formed by four–six methylene groups and taking into account the geometrical relations in a tetrafunctional node. According to the calculation, the number of bonds between entanglements should be 175, which agrees with experiment.

Other attempts to estimate the distances between the entanglements on the basis of geometrical considerations led to different results. Thus it has been found that in a chain comprising 700 units a loop may be formed by a sequence incorporating not less than 30 units.³⁹ The calculation of the density of the entanglements network in the form of loops, carried out using the van der Waals volumes of the molecules and the molecular packing coefficient, led to the conclusion that the effective distance between the loops must be such that the mass of this section would be several times greater than the mass-average molecular mass of the usual polymer.⁴⁰ It was also shown that the formation of loops is unfavourable on thermodynamic grounds as well. Frank-Kamenetskii and Vologodskii (see their review⁴¹) estimated the probability of the formation of loops and rings with a complex configuration. These results are especially important in the consideration of the topological structure of network polymers.

2. The properties of polymers associated with the topological limitations to chain conformations

Allowance for the topological limitations to conformations implies in the first place the abandonment of the hypothesis of phantom chains. The partition function of a network with non-intersecting chains cannot be calculated directly. Various models have therefore come to be widely employed. In particular, it has been suggested that account be taken of the limitations to the number of chain conformations by examining the statistical properties of the chain in the form of an external potential having the form of a 'box' or 'tube'^{42,43} or by introducing the concept of sliding links.^{34,44} It was proposed that the effect of neighbouring chains be modelled on the basis of the elastic potential of the attraction to the equilibrium position — channel.⁴⁵ Another version of the modelling of topological limitations is the approach, which may be called the 'chain in the entanglements lattice'.²⁵ It is usually assumed that the deformation of the surroundings of the chain, modelled by a tube, channel, or entanglements lattice, is of the affine type. The model parameter is as a rule the size of the tube linked in one way or another to the concentration of entanglements. When account is taken of topological limitations, one has in mind small deformations, which makes it possible to analyse the network elastic potential constant W in the form of the Mooney–Rivlin equation:

$$W = C_{100}(I_1 - 3) + C_{010}(I_2 - 3), \quad (1)$$

where C_{ijk} are elastic constants, I_k the invariants of the deformation tensor with $I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2$ and $I_2 = \lambda_1^2\lambda_2^2 + \lambda_2^2\lambda_3^2 + \lambda_3^2\lambda_1^2$, λ_i is the elongation of the specimen along the i th coordinate axis.

An attempt was also made to construct a theory of the elasticity of a chemical network with entanglements over a wide range of degrees of deformation.⁴⁶ The slip link and tube models have been used for the description of topological limitations under the conditions of small and large deformations respectively. The expression obtained for the free energy of deformation includes two terms:

$$\begin{aligned} \frac{F}{kT} = & \frac{1}{2} N_c \left\{ \frac{(1 - \alpha^2) \sum_{i=1}^3 \lambda_i^2}{1 - \alpha^2 \sum_{i=1}^3 \lambda_i^2} - \lg \left(1 - \alpha^2 \sum_{i=1}^3 \lambda_i^2 \right) \right\} + \\ & + \frac{1}{2} N_s \left\{ \sum_{i=1}^3 \left[\frac{\lambda_i^2 (1 + \eta)(1 - \alpha^2)}{(1 + \eta \lambda_i^2)(1 - \alpha^2 \sum_{i=1}^3 \lambda_i^2)} + \lg(1 + \eta \lambda_i^2) \right] - \right. \\ & \left. - \lg \left(1 - \alpha^2 \sum_{i=1}^3 \lambda_i^2 \right) \right\}, \quad (2) \end{aligned}$$

where N_c and N_s are the numbers of chemical cross-links and entanglements respectively and α and η are parameters characterising the extensibility and slip of the chains respectively.

The first term of Eqn (2) corresponds to the deformation of the chemical network and the second to that of the entanglements

network. The parameter N_s is determined from the rubber elasticity plateau modulus and the parameters α and η for real networks have values of about 0.1 and 0.2 respectively.

An attempt has been made to use the replica method to estimate the contribution of the inhomogeneity of the spatial distribution of the density of chemical cross-links to the free energy of the network⁴⁷ and it was concluded that the free energy and hence the mechanical properties of the polymer depend little on the microscopic details in the distribution of cross-links.

Flory proposed⁴⁸ that the entanglements be modelled as limitations to the number of fluctuations of the network nodes. In this model, it is assumed that the stress consists of the stresses due to the phantom chemical network (σ_c) and the stress associated with entanglements (σ_s). The ratio of the contribution of the entanglements to that of the phantom network is defined by the equation

$$\frac{\sigma_s}{\sigma_c} = \frac{\mu}{v} [\lambda K(\lambda_1^2) - \lambda^2 K(\lambda_2^2)] \frac{1}{\lambda - \lambda^{-2}}, \quad (3)$$

where μ and v are the concentrations of the entanglements and active chains respectively, $\lambda_1 = \lambda$, $\lambda_2 = \lambda^{-1/2}$, and

$$K(\lambda^2) = B \left[\frac{B}{B' + 1} + \frac{(\lambda^2 B' + B)(x\lambda^{-2} + B^{-1})}{x} \right].$$

Here

$$B = \frac{(\lambda - 1)(\lambda + 1 - \xi\lambda^2)}{(1 + g')^2}, \quad g = \lambda^2[x^{-1} + \xi(\lambda - 1)],$$

$$B' = \frac{\partial B}{\partial \lambda^2}, \quad g' = \frac{\partial g}{\partial \lambda^2},$$

x is the ratio of the mean square distance between the ends in the phantom network to the mean square fluctuations of the position of the node in the network with limitations, and ξ is a parameter determining the degree of nonaffinity of the change in the limitations domains on deformation.

Theories of the swelling of polymer networks with allowance for topological limitations⁴⁹ and birefringence⁵⁰ have been developed on the basis of Flory's model.⁴⁸ The experimental data on the mechanical properties, swelling, and birefringence of polydimethylsiloxane networks agreed satisfactorily with Flory's model.^{51–54} This model has been used⁵⁵ to determine the contribution of the molecular parameters to the local deformation and orientation. Subsequently attention was turned to the fact that the nature of the topological limitations should depend on the way in which the network is formed. The proposed lattice model made it possible to take into account the influence of the cross-linking conditions.^{56,57}

The complexity of allowance for the topological limitations to the number of chain conformations stimulated interest in the construction of more rigorous models⁵⁸ and also in the investigation of network structures by means of a computer experiment. The influence of entanglements on the fluctuation of a network node has been investigated.⁵⁹ A rank 1 micronetwork with a node functionality of 3 and fixed ends having a length equivalent to 40 units was examined. Some of the predictions of Flory's model were confirmed, but the parameter x depended linearly on the number of units, whereas according to the above model a quadratic law should have held.

The Monte Carlo method has been used to model phantom networks and networks with nonintersecting chains in order to analyse the dependence of the number of elastically active chains, the form factor, and the cyclic rank on the structure of the network and their relation with the modulus of elasticity and the swelling parameters.^{60–62} The topological limitations were taken into account by introducing δ -multipliers, which differentiate the permissible states of the network, into the integrated expressions for the partition functions and the probability of the Markov chains. It was found that in the region of extension the elastic

behaviour of the model network obeys satisfactorily the Mooney–Rivlin equation.

It appears evident that the dynamic properties of polymers over a long time interval are controlled by the entanglements. For example, the relaxation of stress in uniaxially extended polystyrene has been investigated by the small angle neutron scattering method at a temperature above the glass transition temperature.⁶³ It was found that over a short time interval, the relaxation proceeds only on a small scale, in conformity with Rouse's model. If the time interval is long, the relaxation slows down but it is a large scale process. This is followed by the third stage, in which relaxation is independent of the degree of scattering. This stage is attributed to the unwinding of the entanglements.

The ideas concerning the presence of topological limitations have served as a basis of the 'tube' model — the reptation mechanism of the diffusion of macromolecules in concentrated systems.^{64–66} The characteristic break in the curves relating the spin–spin and spin–lattice relaxation of protons to the molecular mass of polydimethylsiloxanes has been explained by the presence of entanglements.^{34,67} Detailed study of the curves for the decrease in free induction in linear and weakly cross-linked polymers^{68,69} also indicated, according to the authors, the presence of a network of entanglements for a molecular mass of the polymer of the order of 10^5 . However, the mechanism of the diffusion of macromolecules was then interpreted within the framework of Rouse's theory: the 'tube' is not manifested in the time interval within which the NMR method operates.

The molecular mass of the chain section between the entanglements nodes (M_e) is usually estimated from the quasi-equilibrium modulus on the rubber elasticity plateau. These data have been presented in a series of books and reviews.^{34,70–74} We may note the existence of a correlation between M_e and the parameters of the chain rigidity, which are estimated, in particular, from the dimensions of the macromolecular coil in a θ -solvent.^{72,73}

In contrast to linear polymers, the topological entanglements in network polymers influence not only the dynamics but also the equilibrium mechanical properties of the specimens. The equilibrium modulus of shear consists of two components above the glass transition temperature: σ_x , determined from the classical theory of rubber elasticity, and σ_n , associated with the topology of the network.^{22,70} The fraction of the 'topological' component then depends on the degree of cross-linking for with low degree of cross-linking networks.⁷⁵ The contribution of trapped entanglements is manifested not only on deformation but also on swelling. Thus the dependence of the rate of transverse relaxation of protons δ in cross-linked polydimethylsiloxane on the degree of swelling q is divided into two characteristic regions.⁷⁶ In the region of low degrees of swelling, the main contribution to the $\delta(q)$ relation comes from the dispersion of the chains in the solvent. For high values of q , the rate of transverse proton relaxation begins to increase and tends to a limit. Effects associated with the presence of trapped topological entanglements are then manifested.

The study of the physical (mainly dynamic) properties of polymers and polymer blends from the standpoint of the reptation models is being continued.^{77–80} A continuously growing number of results, which do not fully agree with the model of reptation diffusion and indicate the need to correct the structureless model of a polymeric body, are being accumulated in this connection. Thus as early as 1975 analysis of the rheological properties of monodisperse and polydisperse polymers led to the conclusion that 'the characteristic features of the viscoelastic properties of high-molecular-mass polymer blends are incompatible with the concept of a single network of randomly entangled macromolecules of different lengths'.⁸¹

Evidently it is necessary to take into account the real structure of the polymer, at any rate to the extent that the intermolecular interactions are manifested in liquids.

III. Localised intermolecular interactions and their role in low-molecular-mass liquids and polymers

1. Intermolecular interactions and their manifestation in low-molecular-mass systems

In order to elucidate the nature of the physical bonds arising from intermolecular interactions and promoting the formation of physical networks in polymer systems, it is possible to employ, as simple models, low-molecular-mass organic compounds in which there are strong intermolecular interaction centres, namely oxygen-containing (hydroxy-, carboxy-, ester, and other groups), nitrogen-containing (amide, amine, and other groups), halogen-containing, sulfur-containing, and other atomic groups capable of undergoing dipole–dipole interactions and of forming hydrogen bonds. Evidently in a condensed state the molecules of such organic compounds are linked to one another by a system of intermolecular interactions into associated species, the topology of which may be most diverse depending on the number (n) and functionality (F) of the IMI centres, their disposition (terminal, central), and the conformational features of the compounds (especially polyatomic ones), including the barriers to internal rotation. The functionality of an IMI centre should be understood as the number of bonds which may be formed one by such centre. For example, the hydroxy-group has the functionality $F = 2$, since it forms two hydrogen bonds — one at the O atom and the other at the H atom. Evidently for $F > 2$ the formation of associated species of the physical network type becomes probable, whereas for $F < 2$ only discrete structures with limited dimensions may arise.

The very fact of the association of organic liquids and in many instances also the topological characteristics of the associated species formed have long been established.^{5,82} In the light of the problem of physical networks, the association of low-molecular-mass organic liquids is of definite interest: its study may help to discover a correlation between the parameters characterising the initial organic molecule as an elementary structural unit in a system of intermolecular bonds and the parameters of the system itself (the physical network). The nature of the IMI centres, their number and functionality, their positions, their intramolecular environment, and their mobility (the barrier to the internal rotation of an atomic group which is a carrier of the IMI centre) belong to the first group of parameters. The average concentration of intermolecular bonds ν , formed at a given temperature T , the average lifetime of the bonds τ , the form of the function $\nu = f(T)$, and the topological type of the IMI system must be assigned to the second group.

Calculations based on the model of volume pair interactions, resorting to data on the frequencies of the atomic vibrations, the frequencies of pair collisions, and the heats of vaporisation, are used for the rough estimation of the parameters $\nu = f(T)$ and τ .^{82,83}

The correlations observed in suitably selected comparison series, which include a large number of organic compounds, serve as the starting point for further systematic analysis of the physical properties of organic compounds. This results in the possibility of establishing which physical properties depend, and to what extent, on the IMI system (the physical network). Properties such as the boiling and melting points and the molecular packing coefficient K_p depend on the intermolecular interactions to the greatest extent. The molecular packing coefficient is determined by calculation⁸⁴ from data on the volume radii and interatomic distances in the molecule, the van der Waals volume of the molecules (V_v), and the molar volume (V_m) calculated from the density and the molecular mass of the substance.^{40,74} By using different comparison series of organic compounds, it is possible to discover the regularities and characteristic features in the formation of the physical networks themselves from the regularities in the variation of the physical properties.^{85,86}

The fundamental studies,^{40,87–89} in which K_p and V_v were calculated and a comparative analysis of these parameters was

carried out in relation to polymers and low-molecular-mass compounds, must be noted.

The results of the analysis of a representative set of data, including about 3000 organic compounds, are presented below.^{85,86} This series includes the homologous series of mono-, di-, tri-, and, in isolated instances, also tetra-functional organic compounds with hydroxy-, carboxy-, nitrile, amide, ester, halide, and other functional groups, which occur in polymers to different extents.

a. Analysis of the set of data on the physical properties of low-molecular-mass organic compounds

Almost all the physical properties of organic compounds are related in one way or another to the strength of the intermolecular interaction. Evidently, the dependence of physical properties on the intermolecular interaction is multiparametric and, even in a series of organic compounds with isotypical IMI centres, for example in homologous series, the variation of several parameters at once is observed. The analysis of physical properties may therefore be successful only if the set of data is sufficiently representative to ensure the possibility of combining organic compounds into large systematic comparison series and of carrying out a multiprogram comparison.

The initial set should include at least several thousand compounds.⁸⁵ Only the boiling point T_b (as a rule at atmospheric pressure), the melting point T_m , and the density (in the vast majority of cases only at room temperature) have been determined for such a number of organic compounds. Other important physical properties, which depend on the intermolecular interactions just as strongly, for example, the viscosity η and the heat of vaporisation ΔH_e , have been measured for by no means all compounds. The quantities T_b , T_m , and K_p have therefore been used as the basic physical properties for systematic analysis, while the parameters η , ΔH_e , and others have been used only in those cases where this appeared possible.⁸⁵

The quantities T_b and T_m are determined by the intensity of the intermolecular interaction at the opposite ends of the temperature range of the existence of organic compounds in the liquid state. The correlation between T_m and the IMI parameters is then complicated in many instances by crystallisation *i.e.* by the appearance of long-range order, which naturally may introduce errors into the analysis of the regularities in the intermolecular interaction unless this factor is specially taken into account. In this sense, the analysis of T_b is more correct.

When the coefficient K_p is employed, one must take into account its very high sensitivity to the shape of the molecules (conformational set). Therefore, in selecting the comparison series, it is essential to fix the shape factor and to compare only molecules with isotypical conformational characteristics.

The selection of the argument for the functions T_b , T_m , K_p or others plays a special role in the analysis of the set of data on physical properties. The van der Waals molecular volume V_v has been proposed as the universal argument.⁸⁵ This choice is justified in the following way. Strong intermolecular interactions of the type of dipole–dipole interactions and hydrogen bonds always occur against the background of weak dispersion forces, the overall energy of which is approximately proportional to V_v . Strong intermolecular interactions are localised strictly within the limits of a definite atomic group. For fairly high values of V_v , the contributions of the 'background' and localised intermolecular interactions are comparable. Therefore, in order to discover the correlations and regularities actually associated with the strong intermolecular interactions, it is necessary to differentiate the latter taking into account the 'background'. Such differentiation can be achieved by analysing relations of the 'physical properties (T_b , T_m , K_p , etc.) – V_v ' type, provided that one assumes, to a rough approximation, that the magnitude of the 'background' is proportional to V_v and the contribution of strong intermolecular interactions for a fixed number of atomic carrier groups in the molecule is independent of V_v .

b. The role of the intermolecular interaction energy

The energy of the intermolecular interaction of functional groups (E), the values of which were estimated from the heats of vaporisation⁹⁰ (ΔH_v) of the corresponding organic compounds containing groups of the given type, are presented in Table 1. Figs 1–3 present the correlations of T_b , T_m , and K_p with V_v in homologous series of organic compounds having the corresponding functional groups. In order to reduce to a minimum the differences between the molecular shapes, only homologues with linear (unbranched) aliphatic chains and functional groups located at the ends of the chains are presented in the figures. Comparison of the data in Figs 1–3 and Table 1 permits the conclusion that the molecular packing density is the physical property which is most sensitive to the strength of the intermolecular interactions estimated in terms of the energy E . The disposition of the $T_b(V_v)$ curves in Fig. 1 is also consistent with the variation of E in Table 1.

The correlation between the $T_m(V_v)$ relation (Fig. 2) and the IMI intensity is complicated by a series of factors, the most important of which is the molecular shape and, for molecules of identical shape — their symmetry. The role of symmetry can be clearly seen on comparing the $T_m(V_v)$ relations for the even and odd members of homologous series: the even members are always characterised by higher T_m . This indicates a high significance of the contribution of the associative structures with a regular disposition of molecules to the establishment of long-range order

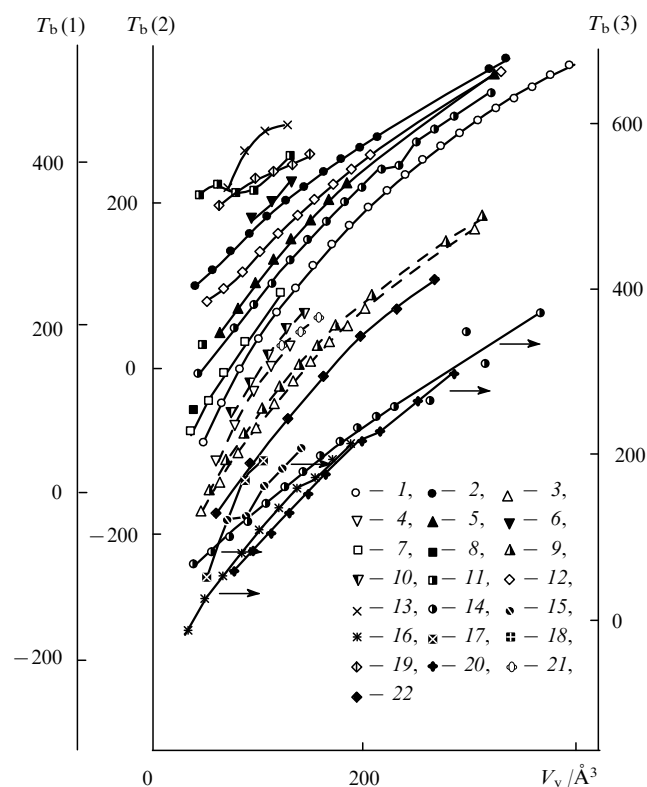
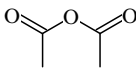
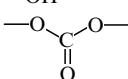


Figure 1. Dependence of the boiling point T_b (in °C) on the van der Waals volumes of the molecules of organic compounds: (1) aliphatic hydrocarbons; (2) monocarboxylic acids; (3) 1-chloro-compounds; (4) compounds dichloro-substituted at chain ends; (5) 1-iodo-compounds; (6) compounds diiodo-substituted at chain ends; (7) 1-fluoro-compounds; (8) compounds difluoro-substituted at chain ends; (9) 1-bromo-compounds; (10) compounds dibromo-substituted at chain ends; (11) amides; (12) nitriles; (13) dinitriles; (14) amines; (15) diamines; (16) aldehydes; (17) dialdehydes; (18) alcohols; (19) glycols; (20) monocarboxylic acid esters; (21) dicarboxylic acid esters; (22) ethers. The dashed curves refer to the $T_b(1)$ ordinate, the continuous curves without arrows refer to the $T_b(2)$ ordinate, and the continuous curves with arrows refer to the $T_b(3)$ ordinate.

Table 1. The energies of the intermolecular interactions of functional groups of different types.

Group	$E/\text{kJ mol}^{-1}$	Group	$E/\text{kJ mol}^{-1}$
—CONH ₂	60.6	CHO—	18.0
—COOH	45.1	—Br	15.9
	35.1		15.1
—C ₆ H ₅	31.8 ^a	—NH ₂	15.1
—OH	30.5	—Cl	13.2
	27.6	—F	7.3
—CN	26.3	—O—	6.3
—I	20.1		2.1
	18.4		

^a The value which does not refer to localised intermolecular interactions but characterises the energy of the dispersion interaction.

on passing from the liquid to the solid state. The contribution of the IMI strength (Table 1) is manifested against this background only as a trend: alcohols, acids, and especially amides, characterised by the highest values of E , occupy a higher position also on the T_m scale. This trend can be seen more distinctly in the region of $V_v > 150 \text{ Å}^3$, where the contribution of the molecular symmetry factor diminishes significantly, which may be inferred from the decrease in the amplitude of the T_m oscillations in the consecutive alternation of even and odd members of the homologous series.

When the molecules contain two functional end groups — carriers of localised IMI centres (see, for example, the data for glycols), the $T_m(V_v)$ curves are sharply displaced upwards relative

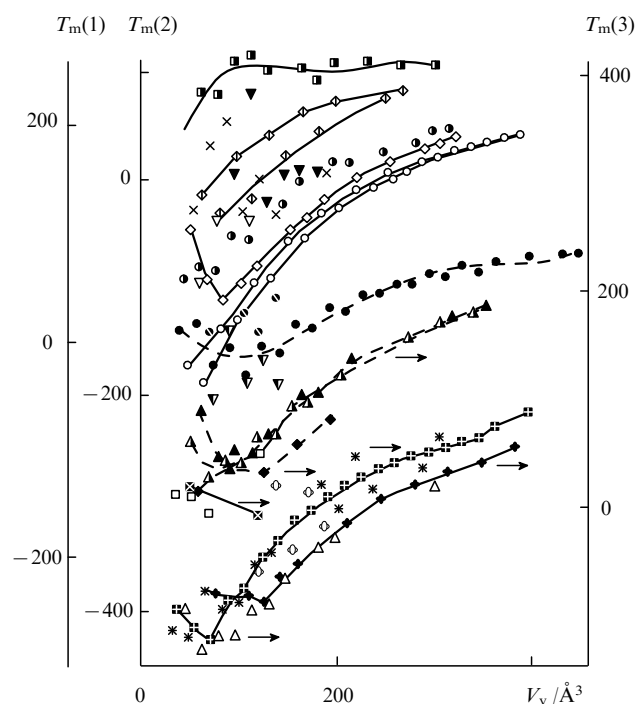


Figure 2. Dependence of the melting point T_m (in °C) on the van der Waals volumes of the molecules (for the designation of the curves, see Fig. 1). The dashed curves and points 7, 10, and 15 refer to the $T_m(1)$ ordinate, points 4, 6, 13, and 14 refer to the $T_m(2)$ ordinate, and the continuous curves with arrows refer to the $T_m(3)$ ordinate.

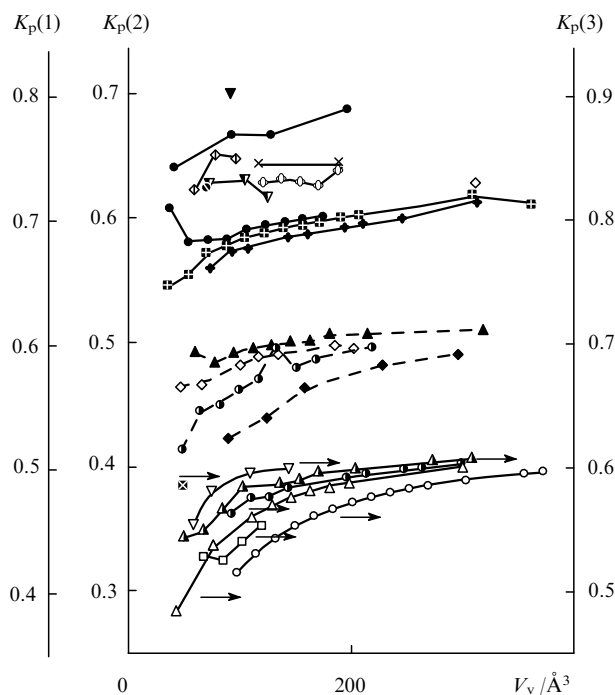


Figure 3. Dependence of the molecular packing coefficient K_p on the van der Waals volumes of the molecules (for the designation of the curves, see Fig. 1). The dashed curves refer to the $K_p(1)$ ordinate, the continuous curves without arrows refer to the $K_p(2)$ ordinate, and the continuous curves with arrows refer to the $K_p(3)$ ordinate.

to the curves for the monofunctional analogues. First of all, this is caused by the increase (doubling) of the average concentration of nodes. The sharp increase in the amplitude of the T_m oscillations for the even and odd compounds indicates the establishment of long-range order: the molecules are arranged in parallel and this arrangement is fixed by the strong terminal intermolecular bonds.

c. The role of molecular shape

Comparison of the IMI-dependent physical properties of molecules with similar values of V_v and E but having different shapes (conformational sets) makes it possible to estimate the contribution of this factor to the formation of the IMI system. As regards organic compounds containing one functional group in the molecule, the analysis leads to the following conclusions.

The molecular shape plays an important role in the formation of associated species both as a purely geometrical factor, promoting (or hindering) close packing and as an intramolecular factor which determines the degree of shielding of the IMI centre by 'inert' substituents. Comparison of the physical properties of isomers of the type $\text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{R}$ (I) and $(\text{CH}_3)_3\text{CR}$ (II), where $\text{R} = \text{OH}$, COOH , Hal , or any other functional group is the carrier of the IMI centre, serves as the simplest illustration. The volumes V_v of different isomers are identical, while the equality of E for the pairs being compared holds owing to the identity of the functional groups. The type (I) linear isomers have a cylinder-like shape, while the type (II) branched isomers have a sphere-like shape. In all cases, the transition from (I) to (II) is accompanied by a sharp rise in T_m in the region of low temperatures, by a decrease in T_b in the region of high temperatures, and by a decrease in K_p in the intermediate region. The shape of type II molecules can exert a dual influence on K_p . On the one hand, it may act as a geometrical factor (the close packing of spheres is looser than that of cylinders). On the other hand, it may also prove to be an intramolecular factor: the shielding of the group R by CH_3 side groups prevents the optimum mutual approach of the groups R of neighbouring molecules, the associative linkages are

weakened, and the packing becomes loosened owing to the decrease in the intensity of the field of intermolecular tightening forces. The occurrence of shielding is confirmed by an appreciable decrease in the heat of vaporisation ΔH_e on passing from form I to form II.

The role of molecular shape at low temperatures is determined by the ability of the system to form regular structures (long-range order). Cooperative intermolecular interactions in such structures lead to a sharp increase in their average lifetime τ up to values comparable to the observation times, which is interpreted as the transition from the liquid to the solid (nonfluid) state. Under these conditions, intramolecular energy barriers, *i.e.* barriers to the rotation of atomic groups around bonds (E_r), as well as the energy barrier to the dissociation of associative (intermolecular) bonds (E), contribute significantly to τ . In essence, the shape of a polyatomic molecule of an organic compound should be understood as a dynamic concept — as the set of conformations characteristic of the given molecule and controlled by the values of E_r .^{91–95} The quantities E_r increase with increase in the number of branches and reach values comparable to E_r . For example, the $\text{CH}_3-\text{C}(\text{CH}_3)_3$ bond is characterised by the quantity $E_r = 19.6 \text{ kJ mol}^{-1}$. In the light of this approach, factors associated with molecular shape, namely symmetry, regularity of the alternation of atomic groups in the molecule, and the values of E_r , should exert, together with E , a decisive influence on T_m . The transition from form I to form II is accompanied by an increase in E_r and in molecular symmetry, which is evidently the actual cause of the sharp increase in T_m .

The replacement of single by multiple bonds in the molecule of an organic compound causes a sharp depletion in the conformational set owing to the extremely marked increase in E_r , which actually leads to the prohibition of rotation about the multiple bond. This entails a corresponding change in the molecular 'shape' and in the physical properties sensitive to the given factor. Comparison of the properties of certain representatives of the classes of acids, alcohols, and aldehydes may serve as a typical illustration (Table 2). The values of E for these compounds are presented in Table 1.

The change in molecular shape in the examples presented, associated with the introduction of multiple bonds, leads to an increase in the molecular packing density: K_p increases on a scale

Table 2. Comparison of the properties of certain typical acids, alcohols, and aldehydes.

Formula	$V_v/\text{\AA}^3$	$K_p^{20^\circ\text{C}}$	$T_m/^\circ\text{C}$	$T_b/^\circ\text{C}$
$\text{CH}_3(\text{CH}_2)_2\text{COOH}$	89.5	0.585	−5.3	163.5
$\text{CH}_3\text{CH}=\text{CHCOOH}$	85.5	0.613	15.5	169
$\text{CH}_3\text{CH}(\text{CH}_3)\text{COOH}$	89.5	0.581	−46.1	154.7
$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOH}$	85.4	0.600	16	163
$\text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{OH}$	87.9	0.578	−89.5	112.4
$\text{CH}_3\text{CH}=\text{CHCH}_2\text{OH}$	83.9	0.597	< −30	121.2
$\text{CH}_3(\text{CH}_2)_2\text{CHO}$	82.2	0.550	−97.1	74.8
$\text{CH}_3\text{CH}=\text{CHCHO}$	78.2	0.569	−69.0	102.2

comparable to the effect associated with the replacement of the relatively 'weak' $-\text{CHO}$ group ($E = 18.0 \text{ kJ mol}^{-1}$) by the very strong $-\text{COOH}$ group ($E = 45.1 \text{ kJ mol}^{-1}$). The increase in packing density is apparently the main cause of the upward shift of both transition points, T_m and T_b , on the temperature scale.

The closure of the chain of functional organic compounds to form a ring also leads to the depletion of the conformational set. Organic compounds with linear and cyclic hydrocarbon chains are characterised by a higher molecular packing density than linear compounds (for $V_v = \text{const.}$). The introduction of multiple bonds into rings increases still further the compaction effect, evidently

owing to the development of additional conformational limitations.

Transition to aromatic cyclic compounds, the molecules of which have a disc shape, extremely favourable for the establishment of the closest packing, does indeed promote a still greater increase in K_p . As an example, one may compare benzene and pentane. Despite its somewhat smaller molecular volume (V_v), benzene has a significantly greater molecular packing density than pentane and hence higher values of T_m and T_b . Cyclopentane, the molecules of which have a similar volume ($V_v = 91.5 \pm 6 \text{ \AA}^3$), occupies, as should have been expected, an intermediate position between benzene and pentane as regards K_p , T_m , and T_b . On passing from pentane to benzene, ΔH_e increases by 6.3 kJ mol^{-1} .⁹⁰ Therefore, in order to discover the actual contribution of molecular shape it is necessary to include in the comparison series an organic compound the molecule of which has a shape similar to that of pentane and ΔH_e higher by 6.3 kJ mol^{-1} than in the case of the latter. Such a compound may be, for example, butyraldehyde (Table 2). It was found that the introduction of the aldehyde group ($E = 18 \text{ kJ mol}^{-1}$), resulting in an increase in ΔH_e by 6.3 kJ mol^{-1} compared with pentane whilst retaining the linear molecular shape, does not lead to an increment in the packing density comparable to that arising on passing from the linear to the disc shape.

Thus the literature data on the properties of organic compounds make it possible to obtain important information for the understanding of the nature of the intermolecular interaction. A more complete study of the intermolecular interaction requires the application of a wide range of experimental methods, among which the traditional approaches occupy an important place:^{5, 82} spectroscopy, measurement of relative permittivity, Rayleigh light scattering, X-ray diffraction, rheology, and thermophysical measurements. Certain new developments^{83, 96, 97} have been designed for the direct experimental determination of the parameters of the IMI system as a physical network — both statistical and with elements of a regular structure. Among these, the main place is occupied by the EPR method in the spin-probe version, which makes it possible to infer from the form of the EPR spectra of nitroxyl radicals in the 3-cm range (without transfer of saturation) the degree of development of a physical network of short-lived associative bonds (τ is 5×10^{-11} to 10^{-7} s) and its evolution as a function of temperature. The spin-probe correlation time is regarded as a measure of the retardation by the physical network of the reorientation process in the magnetic field of the spin-carrying atomic group.

The precision thermomechanical method (sensitivity of 5×10^{-4} mm in terms of deformation), which makes it possible to record the abrupt thermal expansion of the substance at a temperature several degrees below T_m , is also used, provided that the possibility of the formation of a network of physical bonds arises in the system by virtue of the relatively high functionality of the test molecules.

2. Manifestation of intermolecular interactions in polymer systems

a. Molecular packing coefficient in polymer systems

The question of the role of molecular shape and barriers to internal rotation acquires special importance when the information about intermolecular interactions, obtained in the study of low-molecular-mass organic compounds, is transferred to polymer systems. Evidently the repeatability of the shape of the polymer unit as a factor influencing the packing density (and hence the intermolecular interactions and the properties of the polymer depending on the latter) is hindered by the limitation to mobility due to the linking of the units in the chain. This limitation is greater the higher the corresponding barriers to rotation. On the other hand, the limitation to mobility leads to the cooperation of the intermolecular interactions, to an increase in the stability of the IMI system (physical network), and ultimately to an increase in the molecular packing density. Comparison of the set of

properties of polymeric and high-molecular-mass objects, modelling the individual fragments of the macromolecules, yields additional information about the cooperation between the intermolecular interactions in polymers.

In polymers, the units carrying localised IMI centres are linked by covalent bonds. This makes it possible to predict a series of differences between the physical networks in polymers and the similar networks in low-molecular-mass organic substances. Firstly, the degree of cooperativeness of neighbouring physical nodes is greater in polymers, which may be manifested by a sharp increase in their average lifetime τ (by an increase in stability). Secondly, as a result of the linkage of the IMI centres, steric hindrance to their mutual translational approach inevitably arises, which decreases the average concentration of nodes.

Consequently, for identical initial concentrations of the same IMI centres ($2v_0$) in low-molecular-mass organic compounds and in polymers, the nodes of the physical network formed in the latter are more stable (τ is greater), but their concentration v is reduced.

It is noteworthy that the volumes V_v of polymers listed in Table 3 refer to the repeat unit, so that the average volume of the macromolecule is equal to the product nV_v , where n is the average number of units in the polymer chains.

It follows from Table 3 that the molecular packing density of the polymer chains is influenced by the same factors as those influencing the packing density of low-molecular-mass organic compounds (it increases with increase in the IMI intensity and with increase in the barriers to internal rotation, responding to changes in the shape of the macromolecules), but to a much smaller extent. Indeed, the highest and lowest values of K_p [0.684 for poly(vinyl alcohol) and 0.627 for poly(dodecanyl methacrylate)] differ by only 5–6 units in the second digit after the decimal point. On the other hand, if polypropylene ($K_p = 0.669$), the macromolecules of which have exactly the same shape as those of poly(vinyl alcohol), and not the molecules of 'comb-shaped' poly(dodecyl methacrylate) with their outstanding shape, is chosen as the starting point for the calculation, then the difference between the values of K_p is not more than two hundredths.

For low-molecular-mass analogues, the difference between the molecular packing coefficients reaches 0.05 when the limiting value for a hydrocarbon ($K_p = 0.600$ – 0.610) is compared with $K_p = 0.662$ for a dihydric alcohol. If the dihydric alcohol is replaced by a trihydric alcohol, the difference between the values of K_p almost doubles.

It must be assumed that the contribution of the molecular shape factor to the molecular packing density of polymers is significantly greater than for monomers. For this reason, the monotonically constructed hydrocarbon chains $-(CH_2)_n-$ have a fairly dense packing ($K_p = 0.677$) even in the absence of large tightening forces ($E \approx 4.2 \text{ kJ mol}^{-1}$ per CH_2 group). The infringement of the monotonic construction as a result of the appearance of bulky side groups $[-CH_3, -Cl, -OCOCH_3, -COO(CH_2)_nH]$ or the insertion of $-O-$ groups into the hydrocarbon chain, not compensated adequately by tightening forces ($E \leq 16 \text{ kJ mol}^{-1}$), impairs the packing. The compensation phenomenon may be followed in the series of poly(alkylene oxides) (increase in K_p as the $-O-$ groups with $E = 6.3 \text{ kJ mol}^{-1}$ accumulate) and on passing from the $-(CH_2)_n-$ polymer to macromolecules with $-CN$ and $-OH$ side groups ($K_p = 0.677$, 0.681, and 0.684 respectively). When the most bulky $-COO(CH_2)_nH$ substituents are introduced, the packing becomes looser with increase in n not only owing to the operation of the geometrical factor (the shape of the macromolecules) but also because of the characteristic features of the side fragment itself: in relation to low-molecular-mass analogues — dibasic acid esters — the role of the displacement of the IMI centre ($-COO-$) from its position at the end of the molecule to its centre, which leads to a significant increase in K_p , can be clearly traced.

The role of barriers to internal rotation is more marked in polymers than in their low-molecular-mass analogues. Thus, on passing from poly(alkyl acrylates) to poly(alkyl methacrylates), K

Table 3. Comparison of the properties of certain polymers and their low-molecular-mass analogues.

Polymers			Low-molecular-mass analogues		
Formula	$V_v / \text{\AA}^3$	$K_p^{20^\circ\text{C}}$	Formula	$V_v / \text{\AA}^3$	$K_p^{20^\circ\text{C}}$
$-\text{[CH}_2\text{]}_n-$	17.1	0.677	$\text{H}-\text{[CH}_2\text{]}_5-\text{H}$	97.7	0.510
			$\text{H}-\text{[CH}_2\text{]}_{10}-\text{H}$	183.2	0.568
			$\text{H}-\text{[CH}_2\text{]}_{30}-\text{H}$	525.2	0.605
$-\text{[CH}_2-\text{CH}(\text{CH}_3)\text{]}_n-$	51.3	0.669	$\text{H}[\text{CH}(\text{CH}_3)\text{CH}_2]\text{CH}(\text{CH}_3)\text{H}$	98	0.510
			$\text{H}[\text{CH}(\text{CH}_3)\text{CH}_2]_2\text{CH}(\text{CH}_3)\text{H}$	149	0.553
$-\text{[CH}_2-\text{C}(\text{CH}_3)_2\text{]}_n-$	68.5	0.673	$\text{H}[\text{CH}(\text{CH}_3)_2\text{CH}_2]_2\text{H}$	149	0.544
$-\text{[CH}_2-\text{CH}(\text{Cl})\text{]}_n-$	49.1	0.661	$\text{H}[\text{CH}(\text{Cl})\text{CH}_2]\text{CH}(\text{Cl})\text{H}$	93	0.591
$-\text{[CH}_2\text{O}\text{]}_n-$	26.78	0.672			
$-\text{[CH}_2\text{CH}_2\text{O}\text{]}_n-$	43.94	0.679	$\text{H}[\text{CH}_2\text{CH}_2\text{O}]_2\text{H}$	90.2	0.523
$-\text{[CH}_2\text{CH}_2\text{CH}_2\text{O}\text{]}_n-$	61	0.633	$\text{H}[\text{CH}_2\text{CH}_2\text{CH}_2\text{O}]_2\text{H}$	124.4	0.540
$-\text{[CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}\text{]}_n-$	78.1	0.640	$\text{H}[\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}]_2\text{H}$	158.6	0.564
$-\text{[CH}_2\text{CH}(\text{OCOCH}_3)\text{]}_n-$ (PVA)	79.65	0.662			
$-\text{[CH}_2\text{CH}(\text{COOCH}_3)\text{]}_n-$ (PMA)	79.65	0.662	$\text{H}[\text{CH}(\text{COOCH}_3)\text{CH}_2]\text{H}$	154.2	0.630
$-\text{[CH}_2\text{CH}(\text{COOC}_2\text{H}_5)\text{]}_n-$	96.75	0.652		188.4	0.618
			$\text{H}(\text{CH}_2)_m\text{OC}(\text{O})(\text{CH}_2)_n\text{COO}(\text{CH}_2)_m\text{H}$		
$-\text{[CH}_2\text{C}(\text{CH}_3)(\text{COOCH}_3)\text{]}_n-$	96.75	0.682	$n = 3, m = 1$	154.2	0.630
			$n = 1, m = 2$	154.2	0.611
$-\text{[CH}_2\text{C}(\text{CH}_3)(\text{COOC}_2\text{H}_5)\text{]}_n-$	113.85	0.676	$n = 4, m = 1$	171.3	0.628
			$n = 1, m = 2$	171.3	0.616
			$n = 0, m = 3$	171.3	0.603
$-\text{[CH}_2\text{C}(\text{CH}_3)(\text{COOC}_3\text{H}_7)\text{]}_n-$	130.95	0.664	$n = 5, m = 1$	188.4	0.640
			$n = 3, m = 2$	188.4	0.618
$-\text{[CH}_2\text{C}(\text{CH}_3)(\text{COOC}_4\text{H}_9)\text{]}_n-$	148.05	0.663	$n = 6, m = 2$	239.7	0.616
			$n = 4, m = 3$	239.7	0.609
			$n = 2, m = 4$	239.7	0.612
$-\text{[CH}_2\text{C}(\text{CH}_3)(\text{COOC}_6\text{H}_{13})\text{]}_n-$	182.25	0.650			
$-\text{[CH}_2\text{C}(\text{CH}_3)(\text{COOC}_8\text{H}_{17})\text{]}_n-$	216.45	0.639	$\text{H}[\text{CH}(\text{CN})\text{CH}_2]\text{CH}(\text{CN})\text{H}$	137	0.643
$-\text{[CH}_2\text{C}(\text{CH}_3)(\text{COOC}_{12}\text{H}_{25})\text{]}_n-$	284.85	0.627	$\text{H}[\text{CH}(\text{OH})\text{CH}_2]\text{CH}(\text{OH})\text{H}$	78	0.652
$-\text{[CH}_2\text{CH}(\text{CN})\text{]}_n-$	54.0	0.681	$\text{HCH}(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})\text{H}^a$	86	0.705
$-\text{[CH}_2\text{CH}(\text{OH})\text{]}_n-$	41.6	0.684			

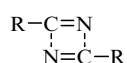
^a Glycerol is not an exact structural analogue of the polymer chain fragment of poly(vinyl alcohol), demonstrating merely the role of the accumulation of hydroxy-groups in the molecule.

increases sharply (from 0.662 to 0.682 for the first members of the corresponding homologous series) owing to the appearance of the methyl side group, which inhibits internal rotation.

b. Network of localised physical bonds

If the polymer contains functional groups capable of forming strong intermolecular bonds, then the latter are a direct source of the appearance of a physical network. According to Flory's classification,⁹⁸ the networks formed by intermolecular physical bonds give rise to an unusual kind of polymer gels, although the difference between polymers with chemical and physical networks is in this instance purely quantitative. In particular, the classical polymer specimen with a chemical network — rubber vulcanised with sulfur at elevated temperatures — possesses the characteristic properties of a polymer with a physical network, namely the capacity for the relaxation of stress and creep, as a consequence of the occurrence of exchange reactions involving polysulfide bonds.^{99, 100}

The dipole — dipole and inductive interactions of the —CN groups in polyacrylonitrile and its copolymers — butadiene-nitrile rubbers — is an example of strong intermolecular interactions leading to the appearance of a physical network. The high dipole moment of nitrile groups makes them capable of forming dimers of the type



with an energy ranging from 19 to 38 kJ mol⁻¹ according to various estimates.¹⁰¹ In the low-molecular-mass analogue of polyacrylonitrile, namely acetonitrile, between 70% and 90% of

the substance is in the associated state. By virtue of the presence of a network of dipole — dipole bonds, polyacrylonitrile has marked rubber-elastic properties above the glass transition temperature and the reversible deformation (before break) may reach 350%.¹⁰¹ In butadiene — nitrile rubbers, an unusual relaxation π -transition corresponds to the disruption of the network of dipole — dipole interactions.^{102, 103}

Another kind of strong intermolecular interaction in polymers is hydrogen bonding. The appearance of hydrogen bonds in polymers is usually caused by the presence of the following functional groups: amides (—CONH) (polyamides, polyester-amides, acrylamide or methacrylamide copolymers), urethane (—COONH) (polyurethanes, oligodiene urethaneepoxides, *etc.*), carboxy- (—COOH) (copolymers of acrylic and methacrylic acids), and hydroxy- (—OH) [poly(vinyl alcohol), cellulose]. The presence of hydrogen bonds in the polymer is deduced from the shift of the absorption frequencies in vibrational spectra,^{104, 105} from the change in the chemical shifts and relaxation times in NMR spectra,¹⁰⁷ and also from the change in the relative permittivities and other indirect data,¹⁰⁸ including the deviation of certain characteristics of monomers from the additive values calculated from atomic group increments.⁷⁴

Numerous studies devoted to polyamides^{105, 106, 109} demonstrated the presence of a strong hydrogen bond in these polymers. Up to 99% of the amide groups form hydrogen bonds in polyamides of certain types. Hydrogen bonds have been detected also in polyurethanes.^{110–112} According to a number of investigators,^{113, 114} hydrogen bonds actually play a role as decisive factor in the mechanical and strength properties of these poly-

mers. Thus comparative study of the IR spectra and viscosities of oligourethane epoxides with different concentrations of urethane and epoxide groups demonstrated that hydrogen bonds are the most important factor responsible for their rheological properties, in particular for the anomalously high viscosity.^{115, 116}

The energy of hydrogen bonds depends on the geometry and nature of the substituents in the groups involved in their formation.^{116–118} Thus it has been shown that aromatic substituents prevent the formation of hydrogen bonds.¹¹⁶ Their replacement by aliphatic substituents leads to partial restoration of the interaction. The high energy of hydrogen bonds imparts to polymers, capable of forming them, all the characteristic features of polymers with a physical network. In particular, the occurrence of transitions in the temperature variation of the modulus of elasticity^{119–121} and the ability to form physical gels^{122–126} have been noted. The physical gels formed *via* hydrogen bonding possess quasi-equilibrium elasticity,¹²⁷ which may be described in terms of the theory of rubber elasticity for sufficiently short observation times. In this instance, the influence of gel formation conditions and of the type of solvent affects the elasticity constant of the gel. The application of a mechanical load leads to partial disruption of the hydrogen bonds, which is reflected in the IR spectra^{108, 121} and is manifested outwardly by the relaxation of stress. In those cases where the groups forming hydrogen bonds are located close to one another in the chain, as happens, for example, in segmented polyurethanes, there is a possibility of the appearance of associated species capable of giving rise even to microphase layer formation. The polyfunctional nodes of the physical network arising under these conditions are especially strong, which imparts the properties of a thermoelastoplastic to the polymer.

Associated species with similar properties may arise also when the polymer contains groups capable of forming bifunctional hydrogen bonds. Thus a polymer in which some of the units form bifunctional hydrogen bonds *via* the COOH- and NHCO-groups has been obtained by the interaction of polybutadiene with 4-(4'-carboxyphenyl)-1,2,4-triazine-3,5-dione.^{125, 126} The formation of associated species leads to the appearance on the corresponding plot of an equilibrium elasticity section with a positive temperature coefficient.

Polyelectrolyte complexes, obtained on mixing aqueous solutions of oppositely charged electrolytes, represent a special class of intermolecular interactions.^{128, 129} A characteristic feature of the thermoreversible gels formed under these conditions is that their modulus and degree of swelling depend on the pH of the medium and on the concentration of low-molecular-mass counterions. By altering the external conditions periodically, it is possible to vary the concentration of the intermolecular bonds and to induce either the contraction or elongation of the specimen,¹³⁰ *i.e.* it is possible to transform chemical energy directly into mechanical energy.

3. Local order and complementary sequences of units

A substance in the polymeric state may form a physical node not only as a result of strong intermolecular interactions, but, as mentioned above, also as a result of the cooperation of weak dispersion bonds. Such interaction leads to the appearance of a short-range order region in the polymer. Although numerous studies have been carried out on the problem of the ordering of polymers in the amorphous state (see, for example, Boyer¹³¹), this question continues to be controversial, mainly because many experimental results used to demonstrate the existence of local order are in principle susceptible also to a different interpretation. This applies mainly to studies on the electron microscopy of polymer films.^{132–136} The existence of local order is indicated, according to a number of workers,^{137–139} by the presence of several distinct 'intermolecular' maxima on wide angle X-ray diffractograms for both noncrystallising polymers above and below the glass transition temperature (T_g) and for crystallising polymers (polyethylene, poly-4-methylpent-1-ene) in the

melt.^{140, 141} The anomalous variation of the heat capacities of polyethylene and polypropylene melts is attributed to the reversible disintegration and restoration of short-range order regions of the smectic type, characteristic of liquid crystals.¹⁴² Convincing data supporting the existence of short-range segmental order in melts of different polymers have been presented in a series of studies.^{143–146} Analysis of the differential curves for radial distribution functions, obtained by electron and X-ray diffraction methods, revealed the existence in melts of crystallising and noncrystallising polymers of sections with a quasi-parallel arrangement of segments with a structure of the liquid crystal type. The dimensions of these sections reach 20 Å in the direction of the long axis of the macromolecule and 30 Å in the perpendicular direction. This result has been confirmed by a careful analysis of the curve for the second moment of the radial distribution function plotted on the basis of X-ray diffraction measurements for a linear polyethylene melt.¹⁴⁷ Three well resolved intermolecular maxima with a periodicity of ~ 5 Å have been observed. Measurements of the osmotic pressures of the solutions and of the heats of solution of polyisobutylene in various solvents permitted the conclusion^{148, 149} that a residual order, corresponding to a degree of crystallinity of the order of $\sim 10\%$, exists in this X-ray-amorphous polymer.

Analysis of the dielectric properties of poly(ethylene terephthalate) in the rubber-elastic state and of polyisobutylene, as well as calculations of the conformations of the macromolecules of these polymers has shown that quantitative agreement between the theoretical dipole moments and other dielectric characteristics is achieved only on the assumption that ordered sections are present in the arrangement of chain segments with a quasi-crystalline structure.^{150, 151} A characteristic feature of the dependence of the most probable relaxation time τ of the dipole-segmental polarisation on temperature is the fact that the slope of the $\lg \tau = f(1/T)$ curve changes within a comparatively narrow temperature range where $T \gg T_g$. This 'liquid-liquid' type transition, observed in many polymers,¹⁵² apparently indicates the cooperative nature of the motion of the segments at $T > T_g$ and its loss above the transition temperature.

The presence of ordered structures has been observed by the light scattering method in vitreous poly(methyl methacrylate)¹⁵³ and by small angle X-ray diffraction in vitreous extended poly(methyl methacrylate), polystyrene, and poly(vinyl acetate).¹⁵⁴ The density of the ordered sections is found to be close to that of the crystal.¹⁵³ Order among the chains in the amorphous regions of linear polyethylene can be observed by pulse ^2H NMR.¹⁵⁵

The idea that highly dense fluctuations (clusters) occur in amorphous polymers served as the basis of the cluster model of the structure of vitreous bodies and of the vitrification process.^{155–157}

A survey of experimental data on the structures of flexible-chain polymers in the amorphous state permitted the conclusion that the appearance of local order is a characteristic feature of the structures of amorphous polymers in the melt.^{158, 159} The approximate agreement between the experimental curve for neutron scattering by deuterated polymer chains and the theoretical curve calculated on the basis of the Gaussian model^{16, 18} does not conflict with the idea that small sections with an ordered arrangement of the segments are present subject to the condition that the distribution of such sections within a macromolecular coil is Gaussian. This claim appears entirely reasonable, particularly since experiment has shown that even strong local interactions, such as chemical cross-linking, do not give rise to an appreciable disturbance of the conformational state of the molecule as a whole.¹⁴ However, this view is not generally accepted and the question of the structures of amorphous polymers remains controversial.^{160–164}

At the same time the existence of local order in a whole series of polymers is unquestionable. For example, complementary syndiotactic sequences of one poly(methyl methacrylate) chain form stable stereocomplexes with isotactic sequences of another chain, which are so strong that this leads to the appearance of

strong physical network nodes,¹⁶⁵ although the bond energy corresponding to each interacting atomic group is only several kJ mol⁻¹.

We may note that the probability P_n of the formation of a complex of n linked groups (of a n -block) is significantly greater than the probability of its formation from isolated groups.¹⁶⁶ Indeed elementary calculation has shown that in the former case $P_n = 1 - (1 - \alpha)^n$, where α is the probability of the formation of a single bond (the complex exists so long as at least one bond remains unbroken), while in the latter case $P_n = \alpha^n$ (the complex exists provided that all n bonds have been formed). Since $\alpha < 1$, the difference is evident.

Similar stereocomplexes arise between the macromolecules of atactic polystyrene.¹⁶⁷ Solvent molecules may participate in their formation, which leads to the formation of thermoreversible gels in 'good' solvents. The structure of these complexes resembles that of a liquid crystal and their fusion is manifested as a temperature transition on differential thermal analysis curves. The temperature transitions in emulsion poly(vinyl chloride) above the glass transition temperature are apparently of a similar nature.¹⁶⁸ Sequences of stereoregular units participate in the establishment of local order, which gives rise to the appearance on the X-ray diffraction patterns of reflections corresponding to a degree of crystallinity of the order of several per cent.¹⁶⁹

The formation of regions with local order in atactic polymers is a special case of the crystallisation of copolymers. As mentioned in a monograph,¹⁷⁰ chemically identical but isomeric units impart a distinct copolymeric character to the crystallisation behaviour of the macromolecule. For this reason, when the crystallisation temperatures of the components of a copolymer or of the isomers of a homopolymer differ sufficiently, then in the range between the melting points of the individual components the units of the higher-melting component exhibit a tendency towards ordering and hence towards the formation of a physical network. The degree of ideality of the crystal structure depends on the ability of the units of the copolymers to become arranged in the form of blocks.¹⁷¹ The possibility of regulating the mechanical properties of the polymer over a wide range appears in this instance. In particular, it has been shown¹⁷² that the thermoviscoelastic properties of ethene-propene polymers can be deliberately varied by altering the diameters of the nodes of the physical network formed by the microcrystallites of the ethene blocks.

The stability of the physical nodes and the mechanical behaviour of the system depend on the degree of local order and on the ideality of the local structure, which may consist of a wide range of formations — from fluctuation regions of the liquid crystal type up to fully regular microcrystallites. The temperature-time conditions in the preparation of specimens influence in their turn the ideality of the local structure and hence are capable of altering the relaxation characteristics of the physical network.¹⁷³

4. Fluctuation inhomogeneity and microphase separation

The inhomogeneity of the supermolecular structure of polymers, understood in a broad sense, is an evident consequence of the molecular inhomogeneity of the polymers and copolymers themselves, arising in the stage involving their synthesis, modification, and cross-linking. First of all, the inhomogeneity is manifested as density and molecular mobility fluctuations, which is recorded by various structure-sensitive methods.^{132, 174–179} Microinhomogeneity can arise also in the stage involving the segregation of polymers as a consequence of the molecular mass distribution and spontaneous fractionation of the macromolecules on coagulation of the latex.¹⁸⁰

Owing to the fluctuations in the concentration of the vulcanising agent, during the cross-linking of elastomers regions differing in the degree of cross-linking and hence in the mobility of their constituent chains appear. This can be detected, for example, by high-resolution ³C NMR.^{181, 182} It has been suggested¹⁸³ that the cooperative relaxation of such densely cross-linked microregions of a network polymer is one of the slowest processes. It may be

that similar processes have been observed in the study of polymer-oligomer blends:¹⁷⁹ according to pulse NMR data, a true equilibrium is established in such systems in the course of tens and perhaps hundreds of hours.

In those cases where the inhomogeneity is of fluctuation type and is not accompanied by microphase layer formation, the difference between the mobilities of chain sections belonging to different regions is small and the physical nodes produced have a comparatively low energy. Such inhomogeneities appear mainly in the form of small relaxation transitions on the temperature variations of the modulus and coefficient of mechanical losses.¹⁸⁴ The situation is different when one is dealing with block and graft copolymers.^{113, 114, 185} The vitreous or crystalline domains of rigid blocks formed as a result of microphase separation represent a kind of polyfunctional physical nodes. Their energy is sufficiently high for the systems to behave like cross-linked rubbers below the melting points of the rigid blocks. Despite the fact that block copolymers are as a rule two-phase systems, the concept of a physical network is apparently applicable to them. At any rate, this claim is valid for a low content of rigid blocks when they still do not form a continuous phase. This is indicated, in particular, by the fact that below the melting points of the rigid blocks such systems have the characteristic properties of an elastomer and the principle of the temperature-time superposition is applicable to them,¹⁸⁵ extending also to temperatures above the melting point of the rigid blocks. However, the rigid blocks must then be characterised by employing an intrinsic reduction temperature. Since the dimensions of the domain are small, it can be regarded, subject to certain assumptions, as a polyfunctional physical node.

The concept of a physical network is used also in the analysis of the mechanical behaviour of more complex systems of block-copolymeric ionomers.¹⁸⁶ These thermoelastoplastics have two physical networks. In weakly sulphurised three-block copolymers of the 'styrene-(ethene-butene copolymer)-styrene' type, one network is made up of rigid polystyrene domains and the other consists of ionic clusters distributed within the polystyrene blocks. An intrinsic temperature transition is characteristic of each network. It is noteworthy that, by virtue of their ability to associate, ionomers exhibit a very distinct tendency to form a physical network. Thus the interaction of butadiene-2-methyl-5-vinylpyridine copolymers with monohalides yields, for a vinylpyridine group content as low as 6%, a product with the properties of a thermoelastoplastic, namely a high strength and elasticity,²⁷ which has been attributed to the association of the ionised vinylpyridine groups to form ionic clusters.

At high concentrations of rigid blocks in block copolymers, the domains form a continuous vitreous polymer phase, whereupon the concept of a physical network loses its significance. This applies also to systems such as interpenetrating polymer networks (IPN),^{187, 188} although the theory of rubber elasticity may be used for the analysis of the network structure in the IPN formation stage.

5. Physical gels. Models of the formation of physical gels

The most important characteristic of elastomers with a physical network, which differentiates them qualitatively from locally homogeneous elastomeric systems, is the ability to form thermoreversible physical gels. The range of questions related to the formation, structure, and properties of physical gels is extremely wide. A series of detailed reviews and monographs have been devoted to various aspects of this problem.^{189–191} In the present section, we shall therefore confine ourselves to questions concerning mainly gels arising as a result of a local intermolecular interaction and which have a direct bearing on the topic of the present review.

There are various views on the causes of the transition of a polymer to a gel-like state. Thus Papkov's concept of gel formation¹⁹¹ is based on the idea of the formation of a gel solely in the region of phase separation, the completion of which is prevented by the high viscosity of the concentrated polymer phase. The gel must therefore be regarded as a nonequilibrium

two-phase system with incomplete layer formation. However, it is difficult to agree with this view. Thermoreversible gels may be formed also under equilibrium conditions. Furthermore, there are fairly numerous examples of the existence of homogeneous physical gels.¹⁹² It is well known that phase separation may occur in the course of the chemical cross-linking of the elastomer also in a thermodynamically good solvent (*v*-syneresis).^{22,70}

Thus gel formation is caused by a local interaction between the macromolecules and phase separation should be regarded as its consequence and not conversely. The gel formation process may be divided into two stages.¹⁹² In the first stage, the formation of weak bonds leads to the appearance of stable aggregates or 'swarms' of molecules.^{192,194} The second stage consists in the binding of the aggregates to one another in the course of their growth and in the formation of a three-dimensional structure. The appearance of hydrogen bonds between gelatin molecules may be the main cause of the formation of aggregates, but in gel formation the nodes are not local bonds but ordered chain sections linked by hydrogen bonds.¹⁹³ This mechanism apparently applies also to other biopolymers.¹⁹⁵

At the same time, there is a region where Papkov's concept of gel formation is fully applicable. In particular, this concerns gels with a nonequilibrium structure formed *via* the spinodal decomposition mechanism. It has been shown¹⁹⁶ that there is a definite solution concentration above which a continuous phase, typical for the spinodal decomposition mechanism, may arise. Spinodal decomposition which has not been brought to the stage involving the complete separation of the system into two coexisting phases may be the cause of the polymer solution setting to a gel. Examples of the application of the theory of spinodal decomposition to gel formation have been published.^{197–200} Thus, in aqueous solutions of poly(vinyl alcohol)¹⁹⁹ and in the poly(vinyl chloride)– γ -butyrolactone system,²⁰⁰ gels are formed in the early stages *via* the spinodal decomposition mechanism.

A special case of the formation of thermoreversible gels is phase separation of the 'liquid–crystal' type, which proceeds *via* a mechanism involving the creation and growth of nuclei. The microcrystallites formed may become the nodes of the physical network of the gel. For example, there are experimental data on the formation of a poly(vinyl chloride) gel with nodes in the form of microcrystallites.²⁰¹ At the same time, it is essential to note that crystallisation as such is not a necessary condition for the formation of a gel. In particular, poly(vinyl alcohol) in an aqueous glycerol mixture affords crystalline gels, whereas in ϵ -methylpyrrolidone it gives rise to amorphous gels.

Single-phase gels are formed as a result of the appearance of the nodes of a three-dimensional network under the conditions of local interactions of the macromolecules with one another. Thus the formation of gels has been noted in cellulose triacetate–nitromethane and cellulose diacetate–tetrachloroethane systems at room temperature.¹²⁶ In the first case, the three-dimensional network arises as a result of the dipole–dipole interactions between the acetate groups, whilst in the second it is a consequence of the formation of hydrogen bonds between the hydroxy-groups.

Interest in the problem of the formation of gels as a result of local intermolecular physical bonds arose after gels of atactic polystyrene were observed in carbon disulfide below room temperature.^{167,202–204} It was found that the heat of gel formation in such systems is from 6 to 26 kJ mol^{−1} which is much less than the heat of formation of isotactic polystyrene gels (113 kJ mol^{−1}), which are known to be crystalline. The nature of the bonds ensuring the formation of gels in these systems has not been fully elucidated. A characteristic feature of such gels is that they are formed also in 'good' (in the thermodynamic sense) solvents. There is a view that gel formation is caused by the appearance of stable stereocomplexes involving solvent molecules.^{167,204}

Another view on the gel formation mechanism in polystyrene solutions²⁰⁵ is that this transition is common to all atactic polymers and occurs as a result of the local 'fusion' of segment–segment contacts *via* the Frenkel' mechanism.⁵ The formation of

gels as a consequence of local intermolecular interaction has been demonstrated in relation to poly(butyl methacrylate).^{206,207} The network nodes in such gels consist of locally ordered regions in which 'suspended' butyl ester side groups participate. Comparison of the enthalpy of the physical cross-linking (37 kJ mol^{−1}) with the enthalpy of the intersegment contact (6 kJ mol^{−1}) shows that six segments participate simultaneously in the formation of a single cross-link. This transition has been recorded by dielectric spectroscopy also in the absence of a solvent.²⁰⁶

The formation of oligocarbamide gels in organic solvents is distinguished by interesting features.²⁰⁸ Whereas the acceleration of the formation process on reduction of temperature is characteristic of other thermoreversible gels, in the given instance acceleration takes place when the temperature is increased. This is explained by the fact that the parallel arrangement of the molecules, treated as rigid rods the required increased mobility of which is attained at temperatures close to T_m , is the decisive stage of the process. In this case, the gel formation process is characterised by the competition between the decrease in the number of physical cross-links with increase in temperature and the appearance of new bonds as a consequence of a more ideal molecular packing.

Analysis showed that in most cases the gel formation process is based, regardless of the phase state, on intermolecular interactions promoting the appearance of a three-dimensional network structure. Many studies have been devoted to polymer gels as networks with nodes of a physical nature.^{209–215} Particular attention was then turned to the nature of the node (microcrystal, another microphase formation, cluster comprising chain sections, *etc.*),^{209,210} its functionality,^{211,212} and the thermodynamics and kinetics of the formation of physical network nodes.^{213–215}

Ferry was one of the first to attempt a theoretical description of the formation of a physical gel.²¹⁶ He began with the analogy between the formation of three-dimensional physical and chemical networks. The Flory–Stockmayer theory was applied to thermoreversible gels.² Assuming that the formation of an infinite three-dimensional network requires the formation of 1–2 bonds per macromolecule, Ferry showed (in good agreement with experiment¹⁹³) that the critical concentration for the formation of a gelatin gel is 1%. A relation between the melting point of the gel and its concentration c was found:²¹⁷

$$\ln c = -\frac{\Delta H}{RT} + \text{const}, \quad (4)$$

where ΔH is the enthalpy of formation of a bond in the gel network and T_m is the melting point.

This relation agrees well with experimental data for gelatin gels, but in the case of readily crystallising gels the relation between the melting point and the concentration is described better by the equation²

$$\frac{1}{T_m} = \frac{1}{T_{m0}} + \frac{R}{\Delta H} (V_1 - k_1 v_1^2) \frac{V_0}{V_1}, \quad (5)$$

where T_m and T_{m0} are the melting points of the polymer in the presence and absence of a solvent respectively, k_1 is the interaction parameter, V_1 and v_1 are the molar volume and the volume fraction of the solvent respectively, and V_0 is the volume of the monomer repeat unit.

A theory has been proposed for the description of the sol–gel transition.²¹⁸ Its essence is as follows. The free energy of the polymer–solvent system is represented by the sum of two terms: $F = F_h + F_b$, where F_h and F_b are the free energies of mixing and formation of the nodes respectively. The critical gel formation concentration is calculated with the aid of the Flory–Stockmayer criterion:

$$\varphi = \frac{1 + \exp(-kT\Delta F_b)}{lf^2}, \quad (6)$$

where l is the number of freely jointed segments in the polymer chain and f is the fraction of segments capable of forming a physical node.

The theoretical curve for the sol–gel transition, calculated from the equation presented, as well as the phase diagram plotted on the basis of the equation of state agree well with experimental data for gelatin gels.

The majority of modern theories of the formation of thermoreversible gels are based on the Flory–Rehner theory of the swelling of polymer networks,² according to which the free energy of the swollen network is represented by the sum of the free energy of mixing of the monomer with the solvent and the elastic energy of the network. According to this theory, the swelling pressure of the gel may be described by the equation

$$P = -\frac{RT}{V_1} [\ln(1 - v_2) + v_2 + \chi v_2^2] - \sigma_v(v_2), \quad (7)$$

where V_1 is the molar volume of the solvent, v_2 the volume fraction of the polymer in the swollen gel, χ the polymer–solvent interaction parameter, and $\sigma_v(v_2)$ the volume modulus of elasticity.

Eqn (7) does not describe by itself the formation of a physical gel. Analysis of experimental data on the swelling of gel-forming polymers led to the conclusion²¹⁹ that the phase transition and the collapse of the physical gel may be described if the interaction parameter χ in Eqn (7) is assumed to depend on v_2 :

$$\chi = \chi_1 + \chi_2 v_2 + \chi_3 v_2^2 + \dots,$$

where χ_i are experimentally determined coefficients. In particular, $\chi = 0.505 + 0.37 v_2 + 0.29 v_2^2$ for a solution of polystyrene in cyclohexane. The postulate that the interaction parameter χ be expressed as a function of v_2 had been put forward also earlier.²²⁰ However, on the whole the above theory must be regarded, despite its qualitative agreement with experimental data on the swelling and phase separation in physical gels, as semiempirical.

Tanaka's theory appears to be logically more complete.^{221, 222} It considers a solution of a polymer each unit of which is capable of forming a physical bond with a unit of another molecule. The polydisperse molecular aggregate arising as a result of the interaction is called a cluster. The free energy of the system consists of the Flory–Huggins free energy of mixing ΔF_{mix} and the free energy of formation of the clusters F_{cl} :

$$F = F_{\text{cl}} + \Delta F_{\text{mix}}, \quad (8)$$

$$F_{\text{cl}} = \sum_{m=1}^{\infty} N_m \mu_m^0, \quad (9)$$

where N_m is the number of clusters in which m molecules are bound and μ_m^0 is the chemical potential of the cluster.

By employing the standard Flory – Huggins procedure for a lattice model, Tanaka calculated the distribution with respect to the number of clusters and obtained an expression for the chemical potential of the solvent. The phase diagram of the system is qualitatively consistent with the experimental data for atactic polystyrene gels.

As a development of the above approach, the case where the gel is formed as a result not only of pair interactions but also as a result of the simultaneous interaction of the segments of several molecules was examined.²²³ This permitted a better description of the weak dependence of the critical gel formation concentration on the molecular mass.

The next step was the formulation of a theory, by Khokhlov,²²⁴ of the swelling of polymer networks in a large amount of solvent, taking into account long range interactions. It was suggested that the free energy of a defect-free network be described by the following expression:

$$F = \frac{NT}{m} \left[\frac{dx^2 + dy^2 + dz^2 - 3}{2} - \frac{2}{f} \ln(dx dy dz) \right] +$$

$$+ NT \left[\frac{Bn_0}{dx dy dz} + \frac{Cn_0}{dx^2 dy^2 dz^2} \right], \quad (10)$$

where N is the total number of units in the network, m the average number of units in the chain between two neighbouring branching points, n_0 the average concentration of the polymer under the initial (θ -state) conditions, B and C are the second and third virial coefficients for the interaction of monomer units, f is the functionality of the branching points, and dx , dy , and dz are the relative deformations of the network along the x , y , and z axes compared with the state at the start of the readings.

The first term describes the free energy of the deformation of the network and the second the free energy of the interaction of the monomer units. In essence, this formula differs from the corresponding formula in Flory's classical theory only by the choice of the start of the readings: here the θ -state was selected as the initial state, whereas in Flory's theory the state of the network in the absence of a solvent is assumed to be the initial state.

Within the framework of Khokhlov's theory, an explanation was obtained for the phenomenon of the collapse of polymer networks, first observed experimentally in 1978 in relation to polyacrylamide gels swelling in an acetone–water mixture.²²⁵ This phenomenon consists in a sharp, frequently abrupt, decrease in the size of the specimen on reducing the temperature or on improving the quality of the solvent. Analysis of the collapse of uncharged networks²²⁵ has shown that it is a consequence of a coil–globule transition in the subchains constituting the network. Such a transition may be both a discrete jump (if the chains are sufficiently rigid or if the specimen is subjected to uniaxial extension) or it may be continuous but extremely sharp.

Experimental and theoretical studies of the collapse phenomenon were developed further.^{226–233} Examination of the elastic properties of swollen polymer networks led to the conclusion that the extension of collapsed networks can induce their transition to the swollen state.²³⁴ An expression was obtained for the stress in a swollen deformed network:

$$\tau = \frac{n_0 T}{m} \left(\sigma - \frac{\alpha^2}{\sigma} \right), \quad (11)$$

where σ is the relative deformation along the z axis and α the relative deformation along the x and y axes.

On slow extension, a jump is observed in the $t(\sigma)$ relation. An experimental test showed,²³⁵ that, for a certain solvent composition and temperature, the gel sucks in spontaneously an enormous amount of the solvent during the extension process and that in an uncharged gel the dependence of the degree of swelling on the applied stress is continuous, whereas in a charged gel the transition to the swollen state takes place abruptly.

6. The properties of polymers in the presence of an effective intermolecular interaction

As already stated above, the deformation of polymer systems does not alter the internal energy if the only type of intermolecular interaction is repulsion due to the mutual in penetrability of the chains. Other types of intermolecular interaction may induce a change in the internal energy on deformation.

In the simplest case, the intermolecular interaction potential may be represented as the sum of the potentials of the central and orientation interactions. The orientation interaction potential is then described by the expression²³⁶

$$P(v) = \frac{B}{2} (3 \cos^2 v - 1), \quad (12)$$

where v is the angle between the directions of the interacting segments and B is a constant.

The interaction of segments of this type can be most simply taken into account by the average field method.²³⁷ The expression obtained for the corresponding elastic potential has the form of a

series in powers of N^{-1} . Calculations have shown²³⁸ that the deviations from the predictions of the theory of entropic elasticity for not unduly open networks can be explained precisely by orientation effects. A quantitative procedure for the determination of the parameters of the orientation of elastomers using the wide angle scattering of X-rays has been proposed.²³⁹ An approach which makes it possible to estimate the contribution of the intermolecular interaction to the relation between orientation and deformation was developed in the same study. Apart from the traditional double refraction method, pulse NMR²⁴⁰ and ^1H NMR (molecular probe spectroscopy)^{241, 242} are also used to estimate the degree of orientation order. An important feature of the orientation order on extension is the orientation phase transition of the liquid crystal type induced by the extension.^{243–249}

In contrast to the orientation interaction, local intermolecular interactions of the physical network type are disrupted in the deformation process. The relaxation of stress in deformed elastomers has been accounted for^{102, 250, 251} by the disruption process and subsequent rearrangement of the physical network. It was assumed that the dependence of the lifetime of a physical node on the stress is described by the familiar Zhurkov disruption law.

A simple mathematical model, based on the physical network concept, which makes it possible to describe qualitatively a wide class of phenomena, including equilibrium and non equilibrium properties, has been proposed.^{247, 248} It is assumed that the concentration of physical nodes diminishes exponentially in the deformed state:

$$v = v_e + (v_0 - v_e) \exp(-kt), \quad (13)$$

where v_0 and v_e are the initial and equilibrium concentrations of the physical nodes. The constant k is expressed by Eyring's procedure taking into account the force due to the deformation of the chains. In this sense, the approach is close to Bartenev's idea, because Eyring's equation may serve as a formal justification of Zhurkov's equation.

Despite the semiempirical nature of the model described, the results obtained with its aid agree well qualitatively with a whole series of experimental facts.

A more rigorous model²⁴⁹ describes the influence of the rearrangement the physical network in a chemically cross-linked elastomer on its equilibrium elasticity and mechanical losses. This model presupposes that the chains contain singular points, between which operate attractive forces with a small radius of action. The calculation of partition functions taking into account additional approximations, associated with the low concentrations of the interacting points, yields the following expression for the stress tensor:

$$\sigma_{kn} = \sigma_{kn}^{(0)} + \frac{3kT}{V} \sum_{i < j} W_{ij} \frac{r_{ijk}^0 r_{ijn}^0}{b_{ij}^2}, \quad (14)$$

where $\sigma_{kn}^{(0)}$ is the stress tensor of the Gaussian network in the absence of physical bonds, r_{ijk}^0 are components of the radius-vector between the i th and j th points in the Gaussian network in the absence of interaction, b_{ij}^2 is the square of the deviation, averaged over the network, of the reciprocal radius-vectors of the interacting points from their positions in the network without interaction, and W_{ij} is the probability of entanglement between the i th and j th points:

$$W_{ij} = q \frac{P_{ij}}{1 + qP_{ij}}, \quad (15)$$

where P_{ij} is the Gaussian distribution of the radius-vectors and q is a characteristic of the intensity of the interaction.

Analysis of Eqn (14) for uniaxial deformation showed that the model examined describes qualitatively the known deviations of the experimental relations from the predictions of the classical theory of rubber elasticity.

IV. Thermodynamic model of the deformation of elastomers in the presence of a physical network

As shown above, ideas concerning the physical network are widely used for the qualitative explanation of the processes associated with the alteration of the supermolecular organisation of polymers due to intermolecular interaction. Here the intermolecular interaction is modelled by physical nodes — formations similar to chemical cross-links but with such a low disruption energy that they can be disrupted and reformed as a result of thermal motion. The average concentration of such nodes may vary during the deformation of the specimen, in contrast to chemical nodes.

In the rubber-elastic state, such systems have specific properties determined, on the one hand, by the presence of entropic elasticity and, on the other hand, by the possibility of a change in the parameters of the equation for rubber elasticity on deformation. The existence of quasi-equilibrium rubber elasticity in systems with a physical network constitutes a most important experimental fact, indicating the occurrence in the systems of at least two kinds of fluctuations of the thermodynamic parameters with different time scales.

The first short-term type of fluctuations corresponds to the establishment of equilibrium in the chains constituting the physical network; the second, long-term type of fluctuations is associated with the rearrangement of the physical network itself. The marked difference between the time scales of thermal fluctuations makes it possible to employ a two-level thermodynamic model for a qualitative analysis of the behaviour of such a system.

Knowing the thermodynamic characteristics of the two-level system, it is possible to determine the thermodynamic properties of this system for constant values of the parameters of the second level and when additional information is available about the second level. One can also take into account the process involving the rearrangement of the supermolecular organisation, provided that the thermodynamic properties of the system with a constant supermolecular structure are known.

Such an approach constitutes the basis of the thermodynamic model of the deformation of polymers developed by the authors of the present review.^{252–261}

1. A two-level model of the physical network

In the formulation of the problem of the deformation of a polymer system, a logical difficulty arises, associated with the fact that the deformation of the physical network may entail not only a change in the concentration of the physical nodes but also a rearrangement of the network at constant concentration. If there are no chemical nodes, a change in the size of the undeformed specimen, *i.e.* plastic deformation, is observed. The components of the specimen deformation tensor cannot therefore play the role of external parameters in this instance.

When the state of a physical network is examined in terms of equilibrium statistical thermodynamics, it is postulated that the deformation of the physical network chains remains constant regardless of the way in which the deformation of the specimen varies under these conditions.

However, it is natural to suppose that when extension from the undeformed state takes place over a period sufficiently short compared with the characteristic times of the rearrangement of the network, then the chain deformation parameters actually coincide with the specimen deformation parameters. The justification of this hypothesis follows from the following simple considerations. The rearrangement of the physical network results in a nonaffine migration of the centres of mass of the macromolecules, compared with the deformation of the specimen as a whole. By virtue of the close packing and the mutual impermeability of the chains, the latter occurs as a result of reptation, the characteristic time of which is known to exceed greatly the time required to attain conformational equilibrium.⁶⁵ Thus, if the lifetime of the physical node is short and the rate of extension is

fairly high, then the equilibrium concentration of the nodes is established for a specified deformation of the chains, which differs little from the deformation of the specimen.

When elastomers contain both chemical and physical nodes, the processes involved in the rearrangement are 'frozen' by the chemical network, as a result of which the chain and specimen deformation parameters must be regarded as identical.

These hypotheses made it possible to obtain an expression for the free energy of a deformed network with a constant number of nodes and also expressions for the average number of nodes of the i th type (having an energy E_i) and an arbitrary stress.

The concentration of nodes g is defined by the following equation:^{252, 259, 261}

$$g = nY(D) = n \frac{D \exp D - \exp D + 1}{(\exp D - 1)^2}, \quad (16)$$

where n is the maximum possible concentration of physical nodes and

$$D = \frac{\Delta E}{kT}. \quad (17)$$

Here ΔE is the free energy of formation of a node, including also the free energy $\psi(\lambda)$ of the deformation of the chains attached to the given node.

The form of the $Y(D)$ relation is illustrated in Fig. 4. Evidently the fastest decrease in the concentration of nodes occurs within a narrow region near $D = 0$, i.e. when the free energy of the deformed chains and the energy required to disrupt a node are equal. This condition determines the characteristic temperature of the disruption of nodes for a given deformation and the characteristic deformation on disruption at a given temperature.

The conventional stress is described by the equation

$$\sigma(\lambda) = 2nY(D) \frac{d\psi(\lambda)}{d\lambda}. \quad (18)$$

The qualitative form of this relation for a network without chemical nodes is shown in Fig. 5 (curve 1). The point λ_0 , at which the stress decreases rapidly, corresponds to the condition $D = 0$ in Fig. 4.

The curve $\sigma(\lambda)$ corresponding to equilibrium conditions has an extremum and bounds the region of the permissible non-equilibrium states of the system for which

$$\sigma > \frac{d\psi}{d\lambda}.$$

In other words, the specimen can exist only in states which correspond to points which are not located below curve 1 in Fig. 5. The boundary points on the ascending section of the curve then refer to equilibrium states and those on the section of the curve with $\lambda > \lambda_k$ refer to pseudoequilibrium states.

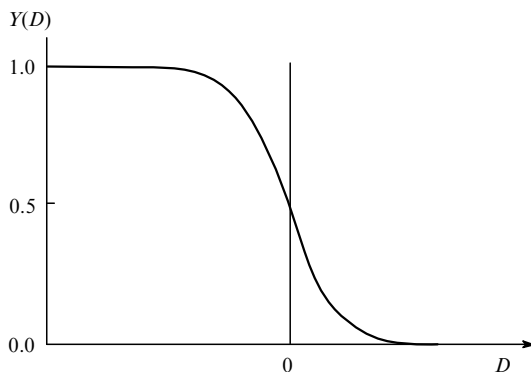


Figure 4. The form of the function $Y(D)$ [Eqn (16)].

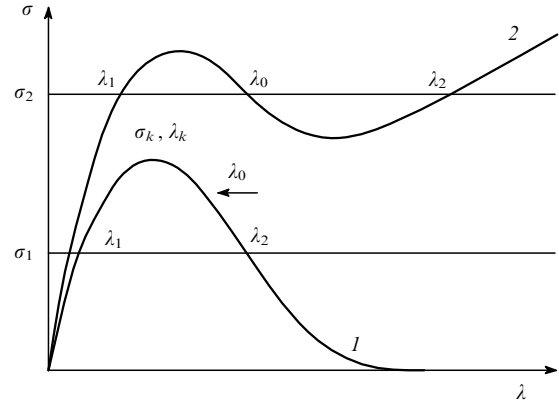


Figure 5. Dependence of σ on λ for noncross-linked (1) and cross-linked (2) polymers (for the explanation, see text).

As can be seen from the figure, the region of permissible states for a specified stress consist of two sections: $[1, \lambda_1]$ and $[\lambda_2, \infty]$. In the absence of thermodynamic fluctuations, the deformation process would end with transition to the equilibrium state λ_1 , since the transition to the non equilibrium region $[\lambda_2, \infty]$ requires that an energy barrier be overcome. However, by virtue of the fluctuations, small fragments of the medium can receive an amount of heat sufficient for transition to the state λ_2 , which leads to irreversible deformation. If the relaxation time of the material to the equilibrium state λ_1 is short compared with the characteristic lifetime of the fluctuations, then in the course of a certain period the specimen is in a state close to equilibrium with a deformation λ_1 and possesses virtually irreversible elasticity. On the other hand, if the external stress exceeds the value corresponding to the maximum on the curve ($\sigma > \sigma_k$), then plastic deformation arises immediately after the application of a load.

Thus the equilibrium theory makes it possible to separate two qualitatively different levels of loads for an elastomer in which there is a physical network. At the first level, for $\sigma < \sigma_k$, there is a possibility of quasi-equilibrium elasticity, while at the second, for $\sigma > \sigma_k$, the disruption of the physical network begins immediately during the deformation process. This feature has become the basis of a method for the determination of the thermodynamic parameters of the physical network nodes from the temperature dependence of their concentration. The concentration of the nodes is calculated from the quasi-equilibrium stress for $\sigma < \sigma_k$, found in experiments on extension at a constant rate or in experiments involving the measurement of creep.

This method has been used in the study of the deformation of elastomers of two classes differing in the mechanism of the formation of physical nodes. The elastomers of the first class consisted of copolymers with functional groups capable of forming fairly strong intermolecular hydrogen bonds.^{259, 261, 262} The objects of study were poly(nonyl acrylate) and its copolymers with acrylamide.²⁶³ The possibility of the formation of physical network nodes in these polymers is attained as a result of the formation of strong hydrogen bonds between the acrylamide or acrylic acid units.

Stereoregular polybutadiene, in which physical network nodes may be formed as a result of the interaction of complementary sequences of stereoregular units, is a representative of elastomers of the second class. Noncross-linked industrial stereoregular SKD polybutadiene and a rubber cross-linked with tetramethylthiuram disulfide were chosen for study.^{257, 261, 264} Acrylamide copolymers were tested under creptation conditions, acrylic acid copolymers were tested in a stress relaxation regime and a regime with extension at a constant rate, while polybutadiene copolymers were tested in a regime 'extension at a constant rate—relaxation at temperatures from -40 to 160 °C'.

It was established that, as the concentration of functional groups increases, there is some increase in the energy of the

physical node due to the change in the nature of the distribution of the functional groups in the chain. Studies by the ^{13}C NMR method showed that the probability of the formation of blocks increases with increase in concentration. The energy of the physical nodes also increases after the additional chemical cross-linking of the elastomer. It was found by ^{13}C NMR relaxometry that this is induced by the decrease in the mobility of fragments of the polymer chains.

An anomalous deformation behaviour is characteristic of elastomers with a physical network: when they are extended at a constant rate, the increase in deformation is sharply retarded after the attainment of a certain deformation up to its complete cessation. In certain cases, the stress can actually fall. In this region, the initial structure is disrupted, which is accompanied by a series of effects such as the appearance of turbidity, a decrease in the Poisson coefficient and the formation of a 'neck', and the appearance of 'string'. On further extension, the stress begins to increase so long as the specimen does not disintegrate, provided that a sufficient number of chains bound in a network retained in the elastomer.

In the presence of chemical nodes, the equation for a conventional stress in the physical network assumes the form

$$\sigma = 2 [nY(D) + n_{\text{chem}}] \frac{d\psi}{d\lambda}, \quad (19)$$

where n_{chem} is the concentration of chemical network nodes.

As can be seen from Fig. 5 (curve 2), the deformation curve has two extrema — a maximum and a minimum. This means that in a certain region two stable states may arise with deformations λ_1 and λ_2 and one pseudo-equilibrium state with a deformation λ_0 for identical values of the conventional stress. Consequently, under these conditions there is a possibility of the separation of the system into regions with different concentrations of the physical nodes and with different degrees of deformation, which is characteristic of a first-order phase transition.

The phase separation arising on deformation of an elastomer with a physical network may explain the characteristic form of the relation $\sigma(\lambda)$ for such systems under the conditions of extension at a constant rate. The section corresponding to a retarded growth of stress on the experimental curves may be compared with the section of the theoretical relation $\sigma(\lambda)$ located between points λ_1 and λ_2 , on which a constant stress should be retained as a consequence of the phase separation on equilibrium deformation.

Under real conditions at a constant rate of deformation, phase separation does not go to completion. For this reason, only a retardation of the growth of stress and not the attainment of a plateau are observed on the experimental curves in most cases. Nevertheless, the observation of the deformation-induced separation into layers with formation of 'string' or a 'neck' in many real polymers in the region corresponding to the section $\lambda_1 < \lambda_0 < \lambda_2$ in Fig. 5 is evidence in support of the validity of the approach under discussion. Furthermore, it is apparently possible to draw an analogy between the deformation-induced separation and the well known phenomenon of the forced elasticity of vitreous polymers. A vitreous polymer can be regarded in a certain sense as a dense-network polymer with physical nodes, because the mobility of chain elements not exceeding in size the kinetic segment is retained below the glass transition temperature. These short chains, whose length corresponds to several units, possess mainly energetic and not entropic elasticity. At the same time, it is quite possible to select for them an expression describing the potential $\psi(\lambda)$. Since it has been shown that the specific form of the potential is unimportant, the relation illustrated in Fig. 5 is qualitatively preserved. The role of the chemical network can be assumed in this case by the network of entanglements, the lifetime of which exceeds by a large factor the lifetime of the low-energy physical nodes constituting the quasi-network of the vitreous polymer. The condition $n > n_{\text{chem}}$ is then known to hold.

The phenomenon of forced elasticity is best illustrated by the deformation-induced layer formation effect. In the first place, the

deformation curve itself, corresponding to forced elasticity, has a distinct horizontal section and sometimes even a bend,^{265, 266} which is fully consistent with Fig. 5. The reversibility of forced elasticity also fits well within the theoretical framework. Finally, the appearance on the $\lambda_1 < \lambda_0 < \lambda_2$ section of 'silver' cracks, which are not cracks in the usual sense but represent layered microregions in the polymer, is also consistent with the concept of deformation-induced separation. In the 'silver' cracks, there is a loosened material with extended chains and a deformation λ_2 , which actually represents a new phase. The chains of the remaining material belong to another phase with a deformation λ_1 . In the course of the cold drawing process, the phase volumes virtually undergo a redistribution: the fraction of the material with the deformation λ_1 diminishes and that of the material with the deformation λ_2 increases. This process continues until the 'neck' has grown by the overall length of the specimen; the phase with the deformation λ_1 then vanishes. Next follows a process in which the chain deformation in the oriented phase increases. The deformation remains fully reversible and, after heating, the specimen again assumes its initial shape.

Naturally, forced elasticity is strictly speaking a nonequilibrium process and all the considerations quoted above must be regarded not as a rigorous theoretical justification but only as an analogy. At the same time, the possibility of an adequate description of the observed phenomena with the aid of this type of extension of the equilibrium theory indicates that it is entirely reasonable.

2. The form of the thermomechanical curve in the region of the rubber elasticity plateau

The proposed equilibrium theory of the deformation of elastomers has served as the basis of the description of thermomechanical curves for linear polymers in the temperature range $T > T_g$.²⁶⁷

The thermomechanical curves for polymers are traditionally analysed on the basis of the concept of a spectrum of relaxation times and their temperature dependence.^{251, 268} An important relation, namely the Williams–Lundell–Ferry (WLF) formula, is actually based on this. The relation between the extent of the rubber elasticity plateau (the temperature range between the glass transition temperature T_g and the flow temperature T_f) and the molecular mass, first obtained by Kargin and Slonimskii²⁶⁹ as early as 1948, can also be accounted for on the basis of a fairly simple model of the relaxation of polymer chains. However, this approach has not so far made it possible to interpret even qualitatively the influence of the molecular mass distribution (MMD) on the form of the thermomechanical curve.^{270, 271} When the WLF equation is used, the temperature dependences of the rates of deformation of polymers with any MMD are of the same kind and the thermomechanical curves differ only in the derivative of deformation, which depends on the average molecular mass.²⁶⁷ Indeed, it has come to be assumed²⁶⁸ that the viscosity of polymer solutions and melts depends on the weight-average molecular mass (or even the molecular mass averaged with respect to higher MMD moments). At the same time, experiment shows that the difference between the deformation curves of polymers with different MMD is qualitative.²⁶⁷

The concept of a network of physical nodes has been used²⁶⁷ for an adequate description of the temperature dependence of the deformation of the polymer in the region of the transition from vitrification to flow.

The theory of the relation between the molecular mass of the polymer and T_f has been based on the dependence of the viscosity on the molecular mass.²⁷² The start of the increase in the derivative of deformation as a function of temperature ($d\varepsilon/dT$) is believed to be a characteristic indication of the transition from the rubber-elastic to the viscofluid state. The application of this feature to a network of physical bonds leads to the conclusion that the increased $d\varepsilon/dT$ is caused by the sharp diminution of the network modulus induced by the disruption of its nodes as a consequence of a rise in temperature. The flow of a polymer

system (at a definite rate of application of a load) begins when the cross-linking index becomes 1.

According to Eqn (16), the concentration of the physical network nodes in the polymer system depends on temperature and the applied force. If the number of nodes is referred to the number of chains N and account is also taken of the fact that the breakdown of the network occurs for fairly large values of D in absolute magnitude, then we obtain the following expression for the critical cross-linking index with respect to physical nodes, *i.e.* for the criterion of the transition to flow:

$$\ln M = D. \quad (20)$$

Bearing in mind that the flow temperature T_f is the same as the glass transition temperature T_g when the molecular mass of the chain is equal to the mass of the segment M_0 , we obtain from Eqns (17) and (20)

$$\ln M = \ln M_0 + \frac{\Delta E}{RT_g} \frac{X}{1+X}, \quad (21)$$

where

$$X = \frac{T_f - T_g}{T_g}.$$

We may recall that the energy term in Eqn (21) takes into account also the intensity and duration of the application of a force to the system. Thus the equation obtained makes it possible to analyse the relation between the temperature of the transition of the system to the viscofluid state, the nature of the load applied to it, and the molecular mass of the polymer.

The relation between the flow temperature and the molecular mass for a series of polymers in terms of the variables of Eqn (21) is presented in Fig. 6. Evidently the equation describes satisfactorily the experimental data. The intercept on the ordinate axis slightly depends on the nature of the polymer (polybutadiene, polyurethanes, polyacrylonitrile) and is close to 3. This means that the molecular mass of the chain section between the physical network nodes is approximately the same and equal to the value for the Kuhn segment in the vicinity of the glass transition temperature of any polymer.^{74, 273} This conclusion is fully consistent with the physical significance of the α -transition: the segmental motion of polymer chains ceases to be inhibited when the length of the chain section between the nodes of the network of physical bonds becomes greater than the Kuhn segment. At the same time the multiplier

$$A \approx \frac{\Delta E}{RT_g}$$

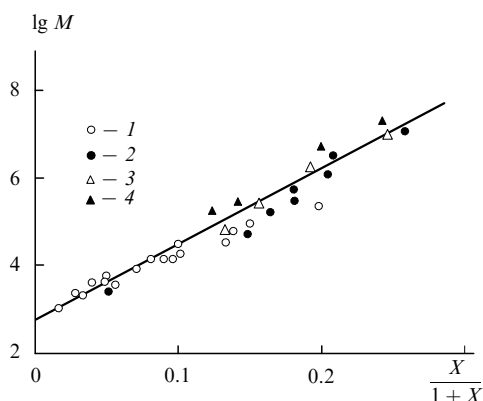


Figure 6. Relation between the flow temperature and the molecular masses of linear polymers in terms of the variables of Eqn (21): (1) polybutadiene; (2) and (3) polyurethanes with different structures; (4) polystyrene.

in Eqn (21) proves to be constant^{272, 273} and almost independent of the type of polymer (the glass transition temperature): $A \approx 17$. Thus Eqn (21) is universal.

Figure 7 presents thermomechanical curves for polybutadienes with different polydispersity parameters.²⁶⁷ Evidently the temperature dependence of the deformation is extremely sensitive to the nature of the MMD. In conformity with the considerations presented above, an increase in temperature induces a decrease in the cross-linking index of the polymer chains and an increase in the fraction of elastically inactive chains of the physical network and in the sol fraction. If the system consists of chains with one length only, then the gel–sol transition occurs at the flow temper-

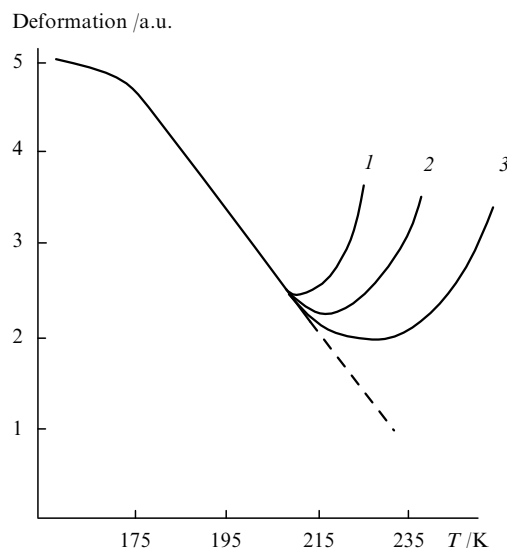


Figure 7. Thermomechanical (dilatometric) curves for polybutadienes with different polydispersities characterised by $M_w/M_n = 1.24$ (1), 3.50 (2), and 9.50 (3). $M_n = 1.45 \times 10^5$.

ature T_f . In this case, the dependence of the proportion of the sol fraction (more precisely of the fraction of elastically inactive chains) ϕ on temperature can be conveniently described using the Dirac δ -function, the integral of which is zero for negative values of the argument and unity for $T - T_f > 0$. Taking this factor into account in the case of a polymer consisting of a set of polymer chains characterised by a distribution function $\omega(M)$, the temperature dependence of the fraction of the elastically active chains ϕ can be described by the equation

$$\phi(T) = \int_0^{\infty} \omega(M) dM \int_{-\infty}^{\Delta M} \delta(t) dt, \quad (22)$$

where $\Delta M = T - T_f(M)$.

The function $\phi(T)$ varies from 0 for $T < T_f$ in the lowest-molecular-mass fraction in the given polymer system to 1 for T_f in the highest-molecular-mass fraction. Thus $\phi(T)$ is an integral function of the MMD when it is constructed not in terms of temperature but in terms of the corresponding molecular masses. We may recall that the relation between temperature and molecular mass is defined by condition (21). Accordingly, the derivative $d\phi(T)/dT$ becomes a differential function of the MMD.

Eqn (22) makes it possible to relate the MMD function to the thermomechanical curve for the polymer if the model is based on the concept of a network of physical bonds. This relation can be formulated in the simplest case as the equation

$$\frac{d\varepsilon}{dt} = \frac{\sigma - [1 - \phi(T)]E\varepsilon}{\eta} \quad (23)$$

or, when account is taken of the linear increase in temperature as a function time,

$$\frac{d\varepsilon}{dt} = \frac{\sigma - [1 - \varphi(T)]E\varepsilon}{\eta q} = \frac{\sigma/E - [1 - \varphi(T)]\varepsilon}{\tau q}, \quad (24)$$

where ε is the deformation, σ the stress, E the modulus of a hypothetical polymer with an infinitely large molecular mass, η the viscosity, $\tau = \eta/E$ the relaxation time, and q the rate of scanning the temperature.

So long as $\varphi(T) < 1$, the deformation occurs in a stationary regime, provided that its rate is sufficiently low. On the other hand, if the rate of deformation is high, a deformation-induced inhomogeneity of the system arises, as mentioned above, which requires a more complex analysis.

Thus the stationary deformation ε_{st} is a measure of the change in the quantity $\varphi(T)$, which increases with increase in temperature:

$$\varepsilon_{st} = \frac{\sigma}{E[1 - \varphi(T)]}. \quad (25)$$

As soon as $\varphi(T)$ reaches unity, the increase in deformation begins to be determined by the differential equation (24), in which the part of the second term enclosed in brackets is 0. At this instant, the decisive factor becomes the temperature dependence of the relaxation time (viscosity) of the system. Thus Eqn (25) establishes a direct relation between the deformation of the polymer system and the integral MMD function $\varphi(T)$.

This conclusion is illustrated by the experimental data in Refs 267 and 275. The approach described made it possible to put forward a method for the determination of the MMD based on the analysis of the temperature variation of the deformation of polymers in the region of the rubber elasticity plateau.²⁷⁵

V. Conclusion

As shown by numerous studies on the structures and properties of polymer systems, a very broad spectrum of intermolecular interactions, ranging from a weak dispersion interaction to a strong dipole–dipole interaction, may be manifested in them. A feature especially characteristic of polymers is that the interaction may involve a fairly large number of bonds (chain units). The presence of long chains predetermines the possibility of the formation of a network of physical bonds, which is reflected in most diverse ways in the properties of polymers.

The physical network model is applicable to the description of the properties not only of systems in which the nodes are formed via hydrogen bonds or a dipole–dipole interaction but also of the properties of crystallising polymers in the rubber-elastic state and also polymers with a complex phase structure, where very dense fluctuations (clusters) may play the role of the microphase. All these formations may serve as physical nodes. Thus the physical network model is in essence applicable to any polymers and polymer systems.

As in any model approach, certain properties of the system are in this instance treated as absolute, their role is over estimated, and other properties are not taken into account. A criterion of the validity of this approach may be its successful application in the solution of the relevant problems. Certain examples of the use of the physical network model in the equilibrium variant have been described.^{255, 258, 259, 276–278} Evidently the theory should answer the question how the structure and properties of the physical network itself vary with time and on what basis one can describe the time variations of the properties of polymer systems. The reptation model of the diffusion of polymer chains is extremely fruitful in this sense. However, it does not take into account the entire diversity of the types of intermolecular interactions in polymers. Certain attempts to take into account this factor theoretically in the study of the dynamic characteristics of

polymer systems have been undertaken.^{261, 279, 280} However, on the whole the problem formulated still awaits its solution.

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^a — *Russ. Colloid. J. (Engl. Transl.)*^b — *Dokl. Chem. (Engl. Transl.)*^c — *Physics-Uspekhi (Engl. Transl.)*^d — *Polym. Sci. (Engl. Transl.)*

Imidazo[1,2-*a*]pyrazines

V A Basiuk

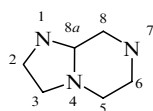
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Abstract. Published data on the methods for synthesis, reactions and natural occurrence of imidazo[1,2-*a*]pyrazines are surveyed. Some other properties and applications of these compounds are also considered. The bibliography includes 273 references.

I. Introduction

The class of imidazo[1,2-*a*]pyrazines (subsequently referred to as imidazopyrazines) comprises heterocyclic compounds based on a fused bicyclic system with a bridgehead nitrogen atom.



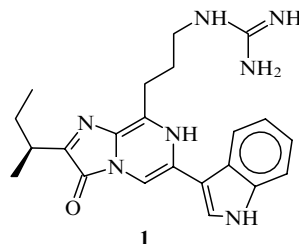
Although these compounds are seemingly simple, they have not been known until recently. The first representative of this class was described only in 1957.¹ However, during the next four decades, the chemistry of imidazopyrazines developed very intensely. Certainly, the attention of researchers was mainly focused on the elaboration of convenient methods for the synthesis of imidazopyrazines and on investigation of their chemical properties, physical properties, comprehensive spectroscopic characteristics and practical applications. A tremendous role in the development of the chemistry of imidazopyrazines belongs to the discovery of several imidazopyrazine-type luciferins that are responsible for the bioluminescence of various sea organisms. This discovery was followed by studies dealing with the elucidation of the structure of these luciferins and of the mechanisms of their bio- and chemiluminescence; these studies differed markedly from those described in traditional publications in the chemistry of imidazopyrazines. Synthesis of the so-called 'azacyclols' (products of cyclisation of activated esters of tripeptides) and other imidazopyrazines containing amino-acid residues as structural fragments was also significant. These studies can be regarded as an impor-

tant link between the chemistry of imidazopyrazines, cyclic peptides and lysergine alkaloids.

The three general lines of research listed above have developed quite independently. If we formally judge the integrity of a field of investigation by the existence of scientific reviews, we find that the published reviews cover mostly the chemistry and the luminescence properties of imidazopyrazine-type luciferins (see, for example, Refs 2–4). To the best of our knowledge, the topic under consideration has been surveyed more broadly only in one review,⁵ which was published in 1979. The above facts stimulated the author to compose a review devoted to the chemistry of imidazo[1,2-*a*]pyrazines. Related fused heterocyclic systems, for example, imidazo[1,2-*a*]quinoxalines,⁶ are not analysed in this review, due to their specific properties and special approaches required for their synthesis. The main purpose of this review was to discuss the methods for synthesis and reactions of imidazopyrazines (*i.e.* purely chemical aspects), whereas in considering their physicochemical features (spectra, structure, reaction kinetics, *etc.*) and practical applications, the author intended to provide readers with only a grasp of the data available from the literature.

II. Natural occurrence

As early as 1917, a bioluminescence reaction was discovered that involved luciferase and a luciferin with an unknown structure, which was isolated from sea crustacean of the genus *Cypridina*.⁷ The structure of luciferin **1** was determined in the middle 60s by high-resolution field desorption mass spectrometry (MS), NMR and amino-acid analysis and was confirmed by its total chemical synthesis.^{8–13}

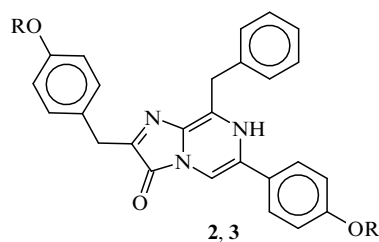


The molecule of coelenterazine **2** also incorporates the imidazopyrazine fragment.^{14–16}

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R = H (**2**), SO₃H (**3**).

Coelenterazine, in turn, is a prosthetic group of the luminescent protein aequorin,^{16,17} which was first isolated from *Aequorea* medusas.¹⁸ Coelenterazine is usually called '*Oplophorus* luciferin', because it can be isolated fairly conveniently from the shrimps *Oplophorus spinosus*. In general, this compound proved to be fairly abundant in the sea fauna. So far, coelenterazine has been found in the tissues of phosphorescent sea organisms, which belong to at least six different classes and range from the relatively primitive radiolaria to fishes.^{19–30}

The third known luciferin, which accounts for the bioluminescence of the cephalopoda mollusks *Watasenia scintillans*,^{15,31,32} is coelenterazine disulfate **3**.

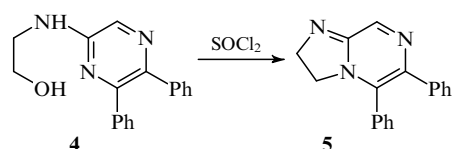
III. Synthesis

1. Construction of an imidazole ring based on pyrazine derivatives

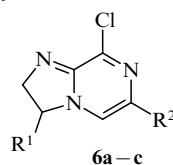
The strategy involving synthesis of an imidazole ring, when a pyrazine ring is already present in the molecule, is most widely used for the synthesis of imidazopyrazines. This approach proved to be especially useful for the preparation of luciferins.

Depending on the nature of functional groups involved in cyclisation, several particular approaches can be distinguished.

The earliest approach to the synthesis of imidazopyrazines was based on cyclisation of *N*-(β-hydroxyethyl)aminopyrazine **4** under the action of thionyl chloride¹ to give 5,6-diphenyl-2,3-dihydroimidazo[1,2-*a*]pyrazine **5**.



Chlorodihydroimidazopyrazines **6a–c** were prepared in a similar way.^{33,34}



6	R ¹	R ²	Yield (%)	Ref.
a	H	Cl	46	33
b	H	H	89	34
c	Me	H	45	34

Cyclisation of oxo-derivatives, obtained by oxidation of hydroxy-derivatives, in the presence of trifluoroacetic anhydride can be regarded as a modification of this method. 2,3-Dehydro-derivatives of compounds **6** were prepared in this way.^{33,34} The scheme for the synthesis of imidazopyrazine analogues of nucleosides, for example, compound **7**,^{35–37} also includes a stage of cyclisation of β-oxoalkylamines involving the N(1) atom of the pyrazine ring (Scheme 1).³⁷

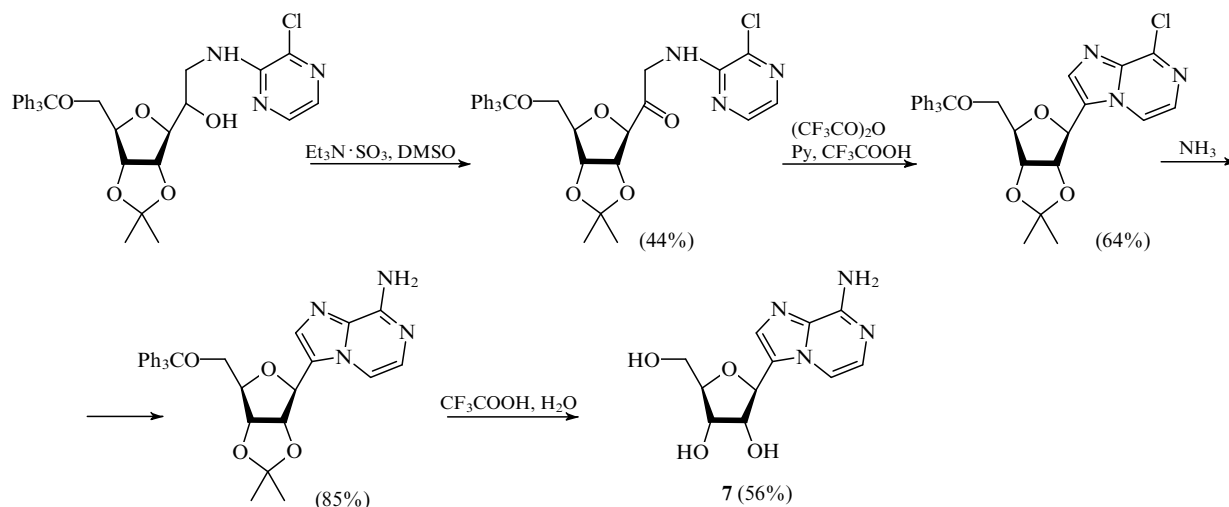
The use of *N*-(β-oxoethyl)aminopyrazine for the preparation of an analogue of 2,3-dihydroimidazopyrazine **5** devoid of phenyl substituents (yield 7%) has been reported.³⁸ The initial compound was introduced in the reaction as diethyl acetal, which was hydrolysed *in situ*.

Total synthesis of the luciferin **1** has been carried out according to Scheme 2.^{10,39}

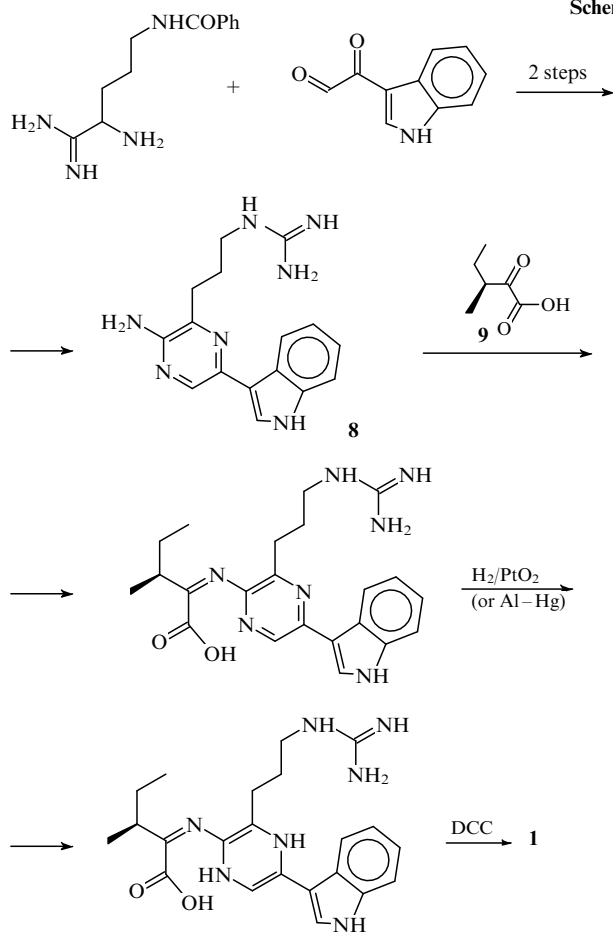
It is noteworthy that beginning from ethioluciferin **8**, the intermediates were not isolated and purified. The yield of the luciferin **1** obtained from ethioluciferin **8** was very low, < 1%.

Construction of an imidazole moiety based on α-oxoacids has also been used to prepare the natural coelenterazine (Scheme 3).⁴⁰ Two modifications of this method were described; according to procedure *A*, α-oxoacid **10** and aminopyrazine **11** were kept in a Bu^tOH–dioxane mixture at 140 °C for 25 min, which gave coelenterazine **2** (yield 49%) together with its dehydro-derivative **12** as a side product (yield 8.4%). According to procedure *B*, a mixture of the initial compounds **10** and **11** was kept in pyridine at 80 °C for 5 h, and this led to a pyrazinyl amino acid **13** in a yield of 49%. Treatment of the latter with a dehydrating agent (for example, Ac₂O) and then by NaBH₄ yielded the coelenterazine **2**.

Scheme 1

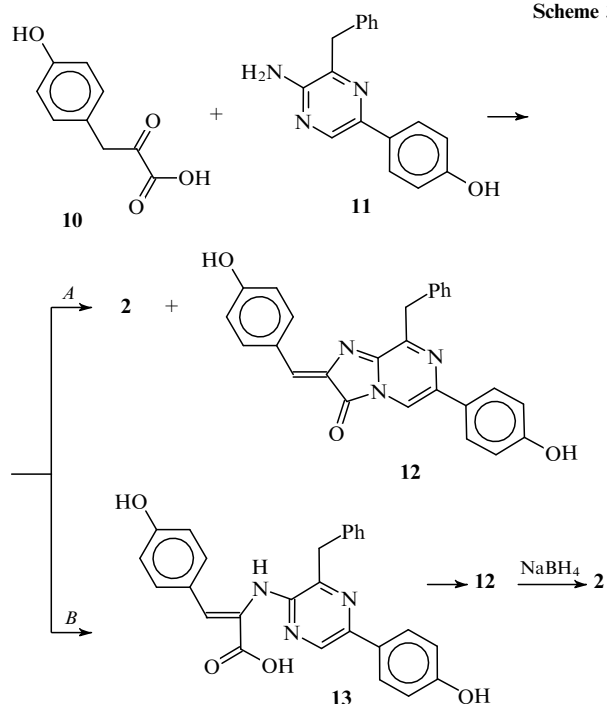


Scheme 2



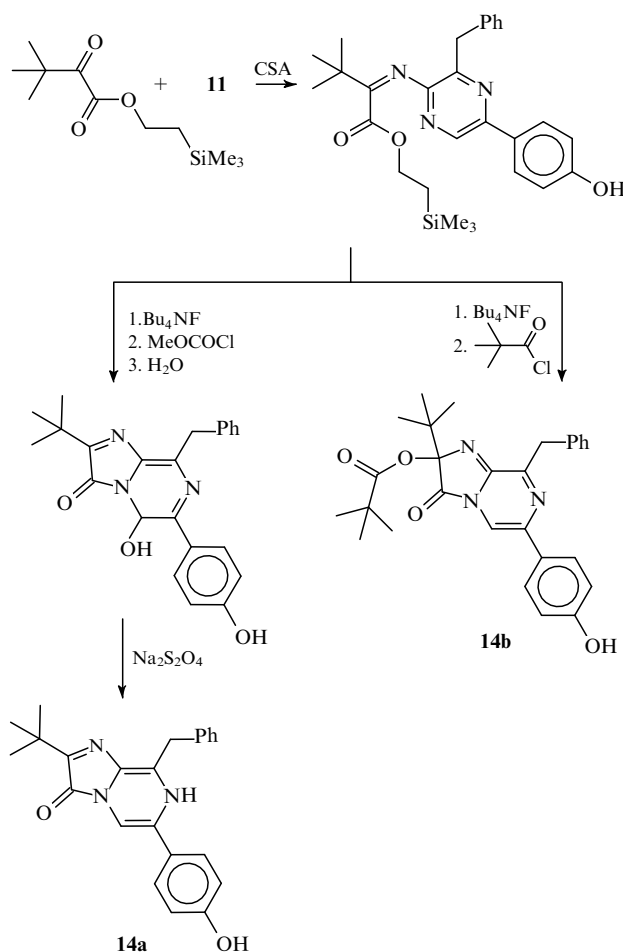
DCC is dicyclohexylcarbodiimide.

Scheme 3



The synthesis of compounds **14a** and **14b** (Scheme 4) in which an ester is used as the dicarbonyl component can be regarded as a specific case of the latter approach.⁴¹

Scheme 4



Where CSA is camphorsulfonic acid.

This approach has received no further development for the synthesis of luciferins or simpler imidazopyrazines.

The procedure for the synthesis of the luciferin **1** was markedly improved when a racemic α -oxoaldehyde, namely, 3-methyl-2-oxopentanal **15** was used in the reaction,^{42,43} instead of the optically active α -oxoacid **9**. As a result, the yield of the luciferin increased to 30%. It is clear that the product obtained in this way exhibited no optical activity. Nevertheless, its bioluminescent activity proved to be nearly the same as that of the natural luciferin.

The same method based on condensation of aminopyrazines with glyoxals^{42–45} made it possible to achieve impressing results in the synthesis of the coelenterazine **2** and its analogues.^{15,41,46–53} The fruitfulness of this approach is clearly demonstrated by the diversity of compounds **16** and bridged analogues of coelenterazine **17** synthesised in this way. The structures of these products are presented in Tables 1 and 2. The bridged analogues **17** are formed in relatively low yields (normally ~10%), whereas the yields of compounds **16** reach 85%.

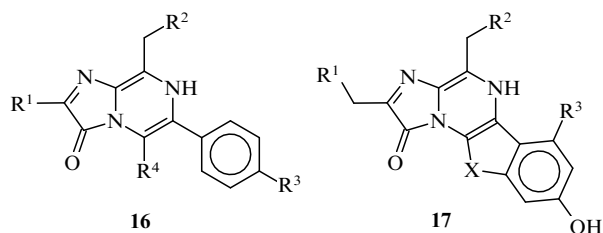


Table 1. Analogues of coelenterazine **16** obtained by cyclisation of aminopyrazines with glyoxals.

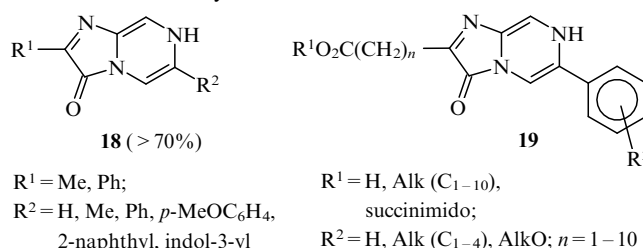
R ¹	R ²	R ³	R ⁴	Ref.
Me	Ph	OH	H	52
Me	Ph	OMe	H	48
PhCH ₂	Ph	OH	H	50
PhCH ₂	Ph	OMe	H	47
<i>p</i> -HOC ₆ H ₄ CH ₂	Ph	OH	H	15, 52
<i>p</i> -HOC ₆ H ₄ CH ₂	Ph	NH ₂	H	49
<i>p</i> -FC ₆ H ₄ CH ₂	Ph	OH	H	51
<i>m</i> , <i>p</i> -F ₂ C ₆ H ₃ CH ₂	Ph	OH	H	50
C ₆ F ₅ CH ₂	Ph	OH	H	50
<i>p</i> -ClC ₆ H ₄ CH ₂	Ph	OH	H	50
<i>p</i> -BrC ₆ H ₄ CH ₂	Ph	OH	H	50
<i>p</i> -IC ₆ H ₄ CH ₂	Ph	OH	H	50
β-C ₁₀ H ₆ CH ₂	Ph	OH	H	50
<i>p</i> -HOC ₆ H ₄ CH ₂	Me(CH ₂) ₃	OH	H	50
<i>p</i> -HOC ₆ H ₄ CH ₂	Pr ⁱ	OH	H	50
<i>p</i> -HOC ₆ H ₄ CH ₂	cyclo-C ₅ H ₉	OH	H	50
<i>p</i> -HOC ₆ H ₄ CH ₂	cyclo-C ₆ H ₁₁	OH	H	50
<i>p</i> -HOC ₆ H ₄ CH ₂	cyclo-C ₆ H ₁₁ CH ₂	OH	H	50
<i>p</i> -HOC ₆ H ₄ CH ₂	<i>p</i> -FC ₆ H ₄	OH	H	50
<i>p</i> -FC ₆ H ₄ CH ₂	Me(CH ₂) ₃	OH	H	50
<i>p</i> -FC ₆ H ₄ CH ₂	Pr ⁱ	OH	H	50
PhCH ₂	cyclo-C ₅ H ₉	OH	H	50
<i>p</i> -FC ₆ H ₄ CH ₂	cyclo-C ₅ H ₉	OH	H	50
PhCH ₂	cyclo-C ₆ H ₁₁	OH	H	50
<i>p</i> -FC ₆ H ₄ CH ₂	cyclo-C ₆ H ₁₁	OH	H	50
<i>p</i> -HOC ₆ H ₄ CH ₂	Ph	OH	Me	50, 51
<i>p</i> -HOC ₆ H ₄ CH ₂	Ph	OH	HO(CH ₂) ₂	51
<i>p</i> -HOC ₆ H ₄ CH ₂	Ph	OMe	H	51
<i>p</i> -HOC ₆ H ₄ CH ₂	Ph	NMe ₂	H	51
Ph	Ph	OH	H	52, 53
Ph(CH ₂) ₂	Ph	OH	H	52, 53
Ph(CH ₂) ₃	Ph	OH	H	52, 53
Bu ^t	Ph	OH	H	41

Table 2. Bridged analogues of coelenterazine **17** obtained by cyclisation of aminopyrazines with glyoxals.

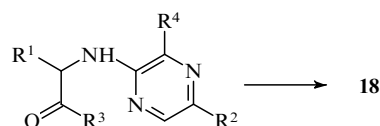
R ¹	R ²	R ³	X	Ref.
<i>p</i> -HOC ₆ H ₄	Ph	H	CH ₂	49, 51
<i>p</i> -HOC ₆ H ₄	Ph	H	CH=CH	49
<i>p</i> -HOC ₆ H ₄	Ph	H	(CH ₂) ₂	49–51
Ph	Ph	H	(CH ₂) ₂	50
<i>p</i> -FC ₆ H ₄	Ph	H	(CH ₂) ₂	50
<i>p</i> -HOC ₆ H ₄	cyclo-C ₆ H ₁₁	H	(CH ₂) ₂	50
Ph	cyclo-C ₆ H ₁₁	H	(CH ₂) ₂	50
<i>p</i> -FC ₆ H ₄	cyclo-C ₆ H ₁₁	H	(CH ₂) ₂	50
<i>p</i> -HOC ₆ H ₄	cyclo-C ₅ H ₉	H	(CH ₂) ₂	50
Ph	cyclo-C ₅ H ₉	H	(CH ₂) ₂	50
<i>p</i> -FC ₆ H ₄	cyclo-C ₅ H ₉	H	(CH ₂) ₂	50
<i>p</i> -HOC ₆ H ₄	Ph	H	(CH ₂) ₃	51
<i>p</i> -HOC ₆ H ₄	Ph	OH	(CH ₂) ₂	51

It can be seen from the above that considerable progress has been achieved in the chemical synthesis of coelenterazine, *Cypridina* luciferin and their analogues. Apparently, it should be expected that this line of research will be further developed. Nevertheless, another trend has appeared, and in the near future it may become a significant alternative to the chemical synthesis: recently, a synthesis of coelenterazine based on genetic engineering technique has been patented.⁵⁴

The method based on the use of α-oxoaldehydes was found to be also convenient for the synthesis of simpler analogues of *Cypridina* luciferin, compounds **18**,^{42–45} as well as of more complex derivatives **19**, which are used as probes for chemiluminescent immunoassay.⁵⁵



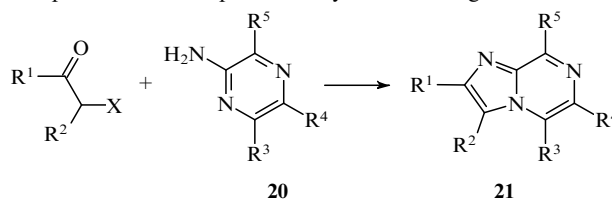
Another approach, which is based on cyclisation of pyrazinyl amino acids, their esters and amides and is similar to that shown in Scheme 1, also gives good results in the preparation of compounds **18**.^{56–58}



R¹ = H, Me, Ph; R² = H, Ph;
R³ = OH, NH₂, OMe, OEt; R⁴ = H, Me.

The method in which aldehydes (as adducts with NaHSO₃) and KCN are used as building blocks for the imidazole fragment has found limited application. For example, it was used to prepare compound **18** (R¹ = R² = H); 3-aminoimidazo[1,2-*a*]pyrazine was formed as a side product.⁵⁹

The method involving α-halocarbonyl intermediates (a special case of the Chichibabin reaction) has found the widest use in the synthesis of simple imidazopyrazines.^{33, 34, 37, 60–87} Generally, this process can be represented by the following scheme:



If the α-halocarbonyl compounds are unstable (in particular, during storage), they can be introduced in the reaction mixture as the corresponding acetals and hydrolysed directly prior to the addition of 2-aminopyrazine **20** (see, for example, Refs 86 and 87). This synthesis is carried out in polar solvents (lower aliphatic alcohols or DMF) and usually with heating, but sometimes at room temperature. To bind the hydrogen halide liberated in the process, Na₂CO₃ or NaHCO₃ is added to the reaction mixture (before mixing of reactants or after completion of the reaction). A large number of imidazopyrazines **21** have been synthesised in this way; some examples are listed in Table 3.

In contrast to the approach described above, the method involving glyoxals, which was used advantageously for preparing luciferins and their analogues, does not enjoy wide popularity, for unknown reasons, in the synthesis of simpler imidazopyrazines. Only few examples describing the use of this method are documented. For example, synthesis of compounds of the type **18** with

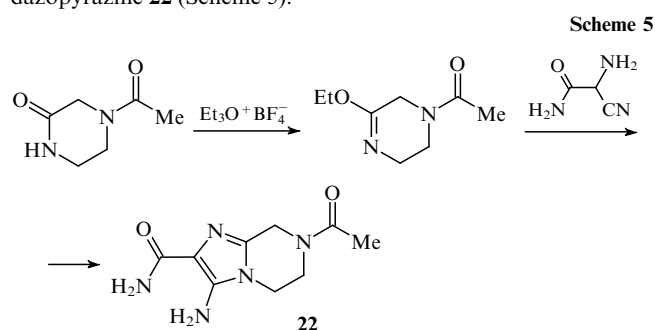
Table 3. Imidazopyrazines **21 a–v** obtained by condensation of α -halocarbonyl compounds with 2-aminopyrazines **20**.

21 (see ^a)	R ¹	R ² (see ^b)	R ³ (see ^b)	R ⁴	R ⁵ (see ^b)	X	Yield (%)	Ref.
a	H	H	H	H	H	Br	41	63
						Cl	39	86
b	H	H	H	Cl	H	Br	68	33
c	H	Me	H	Cl	Br	Br	37	33
d	H	H	H	Ph	Br	Br	73	33
	H	Et	H	H	Cl	Br	59	34
	H	Et	Me	H	Cl	Br	59	34
	Ph	H	H	H	Me	Br	17	34
e	Me	H	H	H	H	Cl	15	61
						Br	20	71
f	H	Me	H	H	H	Br	25	71
						Cl	50	61
	H	H	OH(Cl)	Cl	NO ₂	Br	66	66
	Ph	NO	H	H	H	Cl	55	68
		(NOH)	Cl					
	<i>p</i> -O ₂ NC ₆ H ₄	NO	H	H	H	Cl	60	68
		(NOH)						
g	H	H	H	Br	Br	Cl	45	71
h	CH ₂ Cl	H	H	H	H	Cl	45	71
i	CO ₂ Et	H	H	H	H	Br	30	71
j	H	H	H	H	CO ₂ Et	Br	10	71
k	CO ₂ Et	H	H	Br	Br	Br	40	71
l	CO ₂ Me	H	H	H	H	Br	10	71
m	CH ₂ CO ₂ Et	H	H	Br	Br	Cl	42	71
n	Me	H	H	H	Cl	Cl	37	78
o	Me	H	H	H	PhCH ₂ O	Cl	43	78
p	2,4-(MeO) ₂ C ₆ H ₃	H	H	H	H	Br	6	80
q	2-MeO-4-MeS-C ₆ H ₃	H	H	H	H (CO ₂ Me)	Br	9	80
r	2-MeO-4-MeSO ₂ -C ₆ H ₃	H	H	H	Cl	Br	30	80
s	Me	Me	H	H	Cl	Br	4	82
t	<i>p</i> -MeC ₆ H ₄	H	H	Cl	H	Br	3	83
u	H	MeOCH ₂	H	Br	MeNH	Br	not given	87
v	H	EtOCH ₂	H	Br	MeNH	Br	18	87

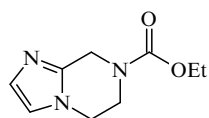
^a Only those compounds which are considered below have been denoted by letters. ^b The substituent in the initial compound **20** is given in parentheses.

R¹ = Ph, *p*-MeOC₆H₄ and *p*-ClC₆H₄ and **R**² = H have been reported.^{88,89} Compounds **21** with **R**¹ = *p*-MeOC₆H₄, **R**² = MeO, **R**³ = **R**⁵ = H, **R**⁴ = Cl (**21w**); **R**¹ = Me, **R**² = OH, **R**³ = **R**⁴ = H, **R**⁵ = OH (**21x**) have also been prepared in this way.^{83,90}

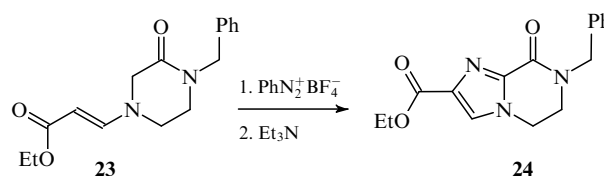
Other methods, in which the imidazole moiety is designed based on a six-membered ring present in the molecule, have been used only in a few studies. For example, treatment of 4-acetylpi-perazin-2-one with triethyloxonium tetrafluoroborate followed by refluxing with α -amino- α -cyanoacetamide gave tetrahydroimidazopyrazine **22** (Scheme 5).^{91,92}



Another representative of the polyhydroimidazopyrazine series has been prepared in a similar way.⁹³



Successive treatment of β -enaminoacrylate **23** with phenyldiazonium tetrafluoroborate and triethylamine yields tetrahydroimidazopyrazine **24**.⁹⁴



Imidazopyrazine **21y** (**R**¹ = Me, **R**² = NH₂, **R**³ = **R**⁴ = H, **R**⁵ = PhCH₂O) has been prepared by the reaction of 2-amino-3-(benzyloxy)pyrazine with acetaldehyde and sodium cyanide.⁷⁸

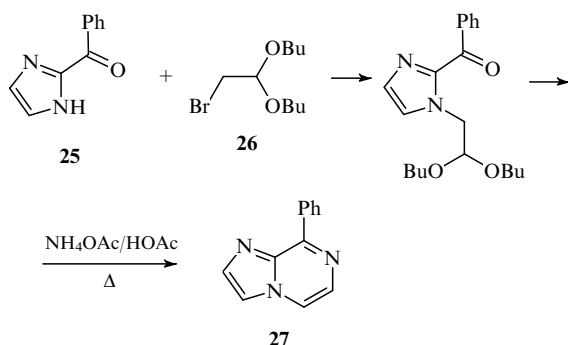
Condensation of 2,3-epoxybutanal with 2-aminopyrazine in the presence of alumina gives rise to 3-(1-hydroxyethyl)imidazo[1,2-*a*]pyrazine **21z** [**R**¹ = **R**³ = **R**⁴ = **R**⁵ = H, **R**² = CH(OH)Me] in 26% yield.⁹⁵

2. Construction of a pyrazine ring based on imidazole derivatives

Condensation of substituted imidazoles is used in the synthesis of imidazopyrazines much more rarely than the strategy considered in the previous Section.^{96–104}

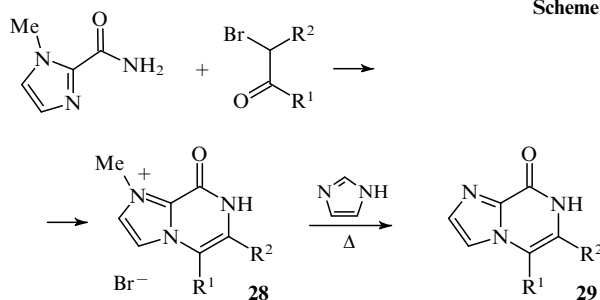
This approach was used for the first time by Russian researchers,⁹⁶ who synthesised 8-phenylimidazo[1,2-*a*]pyrazine **27** in 83% yield by the reaction of 2-benzoylimidazole **25**, which was used as the sodium salt, with bromoacetal **26** with subsequent refluxing of the product with ammonium acetate in acetic acid (Scheme 6).

Scheme 6



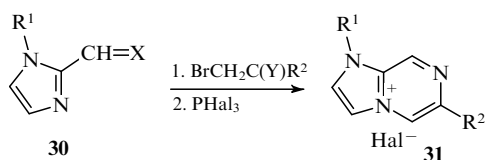
α -Halocarbonyl compounds enter into condensation with 1-alkylimidazole-2-carboxamides^{97,99} to give intermediate imidazopyrazinium salts **28**; the latter can be converted into imidazopyrazin-8-ones **29** by refluxing in imidazole (Scheme 7):

Scheme 7



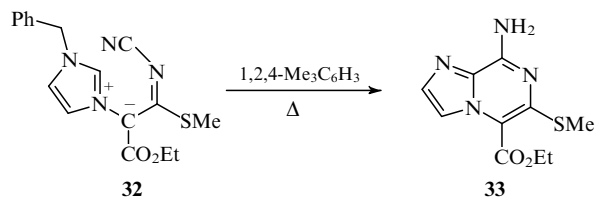
$\text{R}^1 = \text{H}, \text{Alk}, \text{Ph}$; $\text{R}^2 = \text{Ph}, \text{naphthyl}, \text{pyridyl}, \text{furyl}$.

Quaternisation of imidazole-2-carboxaldehyde ethylene acetals and oximes **30** upon treatment with α -halocarbonyl compounds and their oximes followed by deoxygenation of the intermediates thus formed with phosphorus trihalides has resulted in the formation of imidazopyrazinium salts **31**.¹⁰⁰

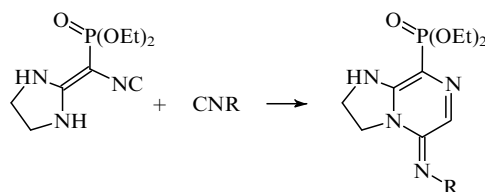


$\text{R}^1 = \text{Me}, \text{PhCH}_2$; $\text{R}^2 = \text{H}, \text{Me}, \text{Ph}$; $\text{X} = \text{NOH}, -\text{O}(\text{CH}_2)_2\text{O}-$; $\text{Y} = \text{O}, \text{NOH}$; $\text{Hal} = \text{Cl}, \text{Br}$.

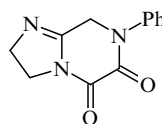
On refluxing in 1,2,4-trimethylbenzene, ylide **32** undergoes 1,6-cyclisation and simultaneous debenzoylation and is thus converted into imidazopyrazine **33**.¹⁰²



An interesting reaction of ketene *N,N*-acetals in which two isocyanide groups participate in the formation of a pyrazine ring has been reported.¹⁰³



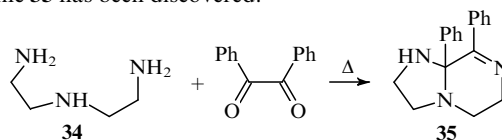
Finally, a 5,6-dioxoimidazopyrazine derivative has been synthesised by interaction of binucleophilic 2-(arylaminomethyl)imidazolines with oxalyl chloride.¹⁰⁴



3. Simultaneous formation of imidazole and pyrazine rings from acyclic precursors

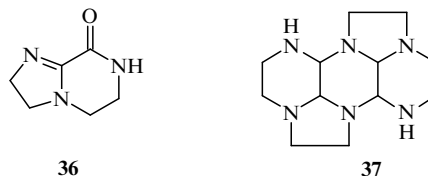
Methods for the synthesis of imidazopyrazines from acyclic precursors are used rather as rarely as those described in Section 2.

Recently, the reaction of diethylenetriamine **34** with dibenzoyl to give 1,2,3,5,6,8*a*-hexahydro-8,8*a*-diphenylimidazo[1,2-*a*]pyrazine **35** has been discovered.^{105,107}

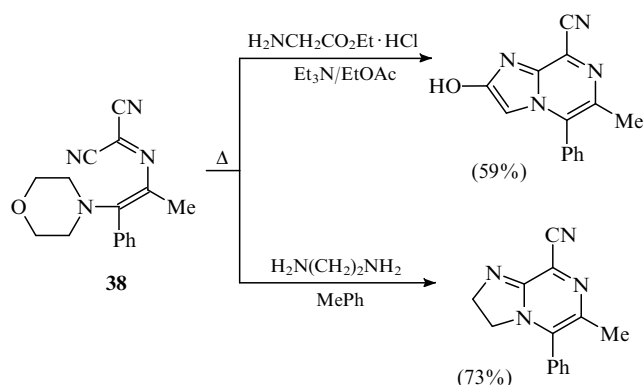


This reaction is carried out by refluxing the reactants in methanol in the presence of mercury(II) chloride (yield 60%).¹⁰⁷

The same amine **34** condenses with diethyl oxalate to give imidazopyrazine **36**,¹⁰⁸ while its condensation with glyoxal or *N,N'*-dicyclohexylethylenediamine affords polycyclic polyamine **37** incorporating two imidazopyrazine structural fragments.¹⁰⁹



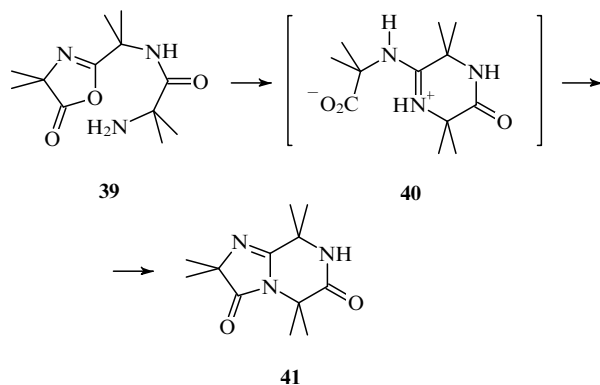
Treatment of ethyleneimine **38** with the ethyl ether of glycine or ethylenediamine gives rise to substituted imidazopyrazines.^{110,111}



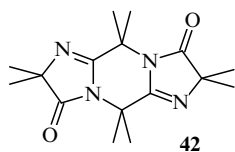
A special position in this group of methods belongs to the preparation of imidazopyrazines from tripeptide (usually linear) derivatives. This approach has been developed within the chemistry of amino acids and peptides, which stands apart from the chemistry of heterocyclic compounds; therefore, terminology peculiar to peptide chemistry has taken root in this line of research.

The formation of imidazopyrazines from derivatives of linear peptides was first described by Jones *et al.*^{112, 113} It was found that the oxazolone derivative **39** of the tripeptide AIB–AIB–AIB (AIB is α -aminoisobutyric acid or α -methylalanine) readily isomerises (in ethyl acetate at room temperature) to give imidazopyrazine **41** in a high yield (95%). This reaction occurs presumably *via* the formation of monocyclic amidine **40** (Scheme 8).

Scheme 8



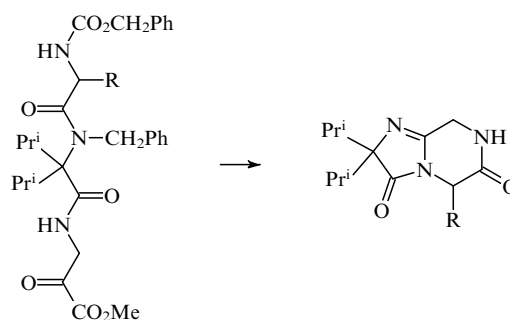
A conceptually similar method for the synthesis of the imidazopyrazine **41** involves treatment of AIB tri-, tetra- and penta-peptides with phosphorus pentachloride or thionyl chloride in acetyl chloride and subsequent cyclisation of the intermediate acid chlorides in pyridine.^{114–117} The yields of the compound **41** obtained in this way are much lower (11%–26%). It is of interest that when tetra- and penta-peptides are used in this reaction, bis-imidazopyrazine **42** is formed simultaneously in a yield of 4%–10%.



This method has also been used to prepare polydeuterated analogues of **41** and **42**.^{115, 116}

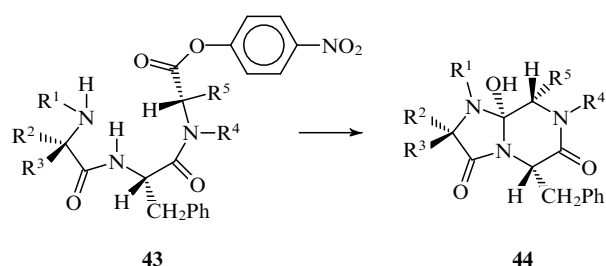
The reactions described above reflect the specific stereochemistry of derivatives of α, α -dialkylamino acids (in particular, AIB), namely, a certain conformational rigidity of their carbon skeleton, and are not characteristic of ordinary natural amino acids. Nevertheless, methods for the preparation of the imidazopyrazines **41**

containing Gly, Ala, Val, *etc.* as structural fragments have been developed. For example, catalytic hydrogenolysis of carbobenzoxy-derivatives of methyl esters of tripeptides¹¹⁸ makes it possible to synthesise the imidazopyrazines of the type **41** incorporating Gly, Ala, Val, Leu and Phe residues.



$\text{R} = \text{H}, \text{Me}, \text{Pr}^i, \text{Bu}^i, \text{CH}_2\text{Ph}$.

Cyclisation of activated esters of tripeptides has been studied in detail by Italian researchers.^{119–128} However, although the compounds obtained in these studies belong to the same class of imidazo[1,2-*a*]pyrazines, they possess an important feature distinguishing them from the amidines **41**: their molecules incorporate a $\text{C}(8a)\text{OH} - \text{N}(1)\text{R}^1$ fragment instead of the $\text{C}(8a) = \text{N}(1)$ fragment. Therefore, these compounds were called 'azacyclics'. As a rule, they are synthesised starting from 4-nitrophenyl esters of tripeptides **43**. According to a typical procedure, tripeptide **43** is kept in a 1 : 1 mixture of dioxane and an aqueous carbonate buffer solution (0.1 M NaHCO_3 + 0.1 M Na_2CO_3 , 1 : 1) for 1–2 h at room temperature. Characteristics for a number of imidazopyrazines **44** obtained in this way are listed in Table 4.



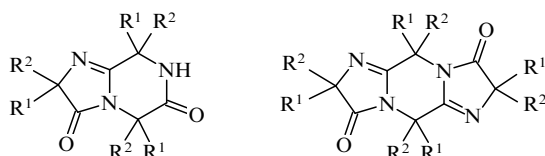
Undoubtedly, it is the mild conditions used in this reaction that account for the preservation of the $\text{C}(8a)\text{OH}$ group in the molecule; otherwise (at elevated temperatures) one should expect that elimination of a water molecule would occur to give the amidine analogues of **41**.

Table 4. Azacyclics **44** obtained by cyclisation of *p*-nitrophenyl esters of the tripeptides **43**.

R^1	R^2	R^3	R^4	R^5	Yield (%)	Ref.
PhCH_2OCO	Me	H	$-(\text{CH}_2)_3-$		70	119
<i>p</i> - $\text{BrC}_6\text{H}_4\text{CH}_2\text{OCO}$	Me	H	$-(\text{CH}_2)_3-$		50	119
PhCH_2OCO		$=\text{CH}_2$	$-(\text{CH}_2)_3-$		80	120
$\text{CH}_2=\text{CHCH}_2\text{OCO}$	Me	H	$-(\text{CH}_2)_3-$		45	121
PhCH_2OCO	Me	H	$-(\text{CH}_2)_2-$		not given	122
PhCH_2OCO	Me	H	Me	H	—	122
$-(\text{CH}_2)_3-$ ^a		H	$-(\text{CH}_2)_3-$		8.5	123
H^a	Me	H	$-(\text{CH}_2)_3-$		—	124
$-\text{COCH}_2\text{SCH}_2-$ ^b		H	$-(\text{CH}_2)_3-$		50	125, 126

^a As a salt with CF_3COOH . ^b In the initial tripeptide, $\text{R}^1 = \text{ClCH}_2\text{CO}$, $\text{R}^3 = \text{CH}_2\text{SSBu}^t$; the protection was removed *in situ* during the cyclisation (Bu_3P and NaHCO_3 in aqueous propanol).

Taking into account the fact that amino-acid residues are the main structural units of the molecules **41** and **44**, it would be reasonable to suggest that these imidazopyrazines could, in principle, also be obtained by intermolecular cyclisation of amino acids or their activated derivatives. However, syntheses of the imidazopyrazines **41** and **44** based on this strategy have not yet been developed. Nevertheless, in a study of the products of high-temperature (200–250 °C) condensation of vaporised amino acids (Ala, Val, Nva, and Leu) catalysed by silica gel,^{129–131} some compounds, dehydrated to a greater extent than cyclic dipeptides (piperazine-2,5-diones), have been detected. The latter are often called ‘amino acid anhydrides’, because they can be obtained directly from amino acids (although this is seldom used for practical purposes). Hydrolysis of these compounds leads to the recovery of the amino acids. Whereas the formation of piperazine-2,5-diones is accompanied by elimination of one water molecule per amino acid molecule (the same 1 : 1 ratio is retained in the case of other cyclic peptides), the products under consideration^{129–131} were found to be dehydrated to a greater extent than the corresponding piperazine-2,5-diones. The ratio of the number of amino-acid residues constituting these molecules to the number of water molecules eliminated upon dehydration is 3 : 4 and 4 : 6. Studies carried out by fast atom bombardment mass spectrometry,¹²⁹ HPLC/MS and GLC/IR/MS with computer simulation of the IR spectra^{130, 131} have permitted these compounds to be identified as imidazopyrazines and bis-imidazopyrazines.

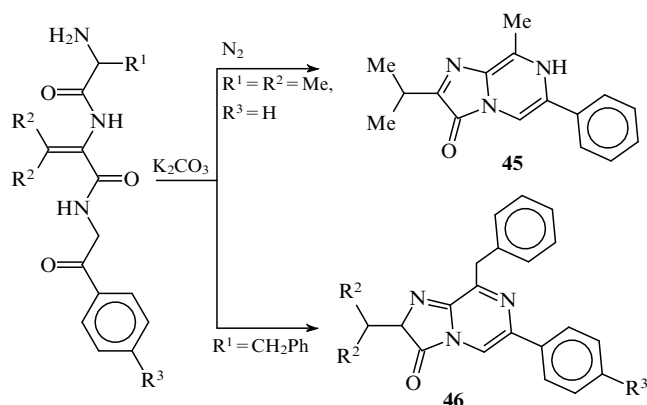


$R^1 = \text{H}$, $R^2 = \text{Me(Ala)}$, $\text{Pr}^i(\text{Val})$, $\text{Pr}^n(\text{Nva})$, $\text{Bu}^t(\text{Leu})$.

The AIB derivatives **41** and **42** ($R^1 = R^2 = \text{Me}$) mentioned above also belong to this class of compound. According to tentative estimates, the yield of imidazopyrazines can reach 20%; however, they are strongly contaminated by products of thermal destruction that occurs immediately after their formation. Thus, the reactions in question can hardly be of any synthetic value.

Some studies, mostly directed at the modelling of the biosynthesis of the imidazopyrazine-type luciferins, have been reported.^{132, 133} The researchers suggested that modified tripeptides are biosynthetic precursors of all luminescent systems (coelenterata, crustacean, etc.). This suggestion was supported by the successful synthesis of compounds **45**¹³² and **46**¹³³ — analogues of the *Cypridina* luciferin and of coelenterazine — carried out according to Scheme 9.

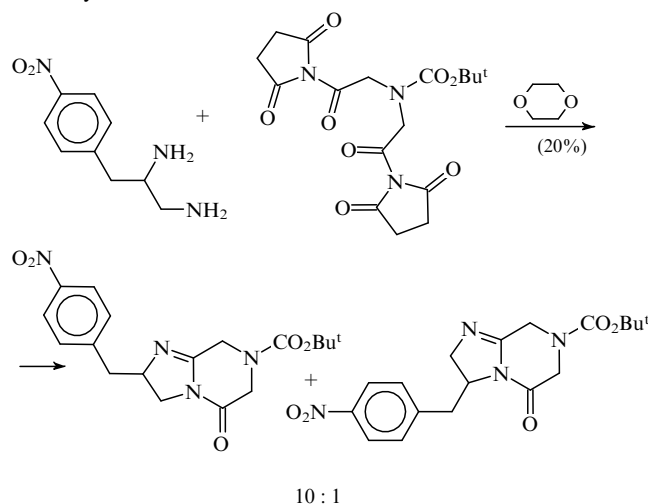
Scheme 9



$R^2 = \text{Me}$; $R^3 = \text{OCH}_2\text{Ph}$, OH , H ;
 $R^2 = \text{H}$; $R^3 = \text{OH}$, H .

A typical procedure consists in heating of tripeptide-like compounds in DMF in the presence of K_2CO_3 . In the case of the compound **45**, cyclisation was carried out under an inert atmosphere (N_2 ; yield 58%).

The last case the author is aware of, where the imidazole and pyrazine rings are formed simultaneously from acyclic precursors is rather an occasional observation in the field of synthesis of polyaza-containing macrocyclic ligands. Condensation of (4-nitrobenzyl)ethylenediamine with N,N' -[*N*-(*tert*-butoxycarbonyl)iminodiacetyl]disuccinimide afforded a mixture of two isomeric imidazopyrazines instead of the expected 9-membered macrocyclic diamide.¹³⁴



4. Introduction and modification of substituents in the imidazopyrazine nucleus

Halogenation^{33, 34, 71, 86, 135, 136} of the imidazopyrazine nucleus is the most important reaction among those involving the imidazopyrazine system, since it permits not only introduction of halogen atoms into this nucleus but also their subsequent replacement by other substituents.

Treatment of unsubstituted imidazo[1,2-*a*]pyrazine (**21a**; Table 3) with bromine in glacial acetic acid results in its bromination in the 3- and 5-positions.^{71, 135, 136} The yields of 3-bromo-, 5-bromo- and 3,5-dibromo-derivatives are 5%, 81% and 5%, respectively.⁷¹

Better selectivity is achieved with *N*-bromosuccinimide. Using the imidazopyrazines **21a** and **21g** as examples, it has been shown that bromination involves the 3-position, the corresponding products being formed in 44–72% yields.^{86, 136} However, when *N*-bromosuccinimide is made to react with 8-(4-*tert*-butoxycarbonylpiperazino)imidazo[1,2-*a*]pyrazine,³⁴ substitution at C(5) predominates (the yield of the 5-bromo-derivative is 55%), and only with excess *N*-bromosuccinimide is the 3,5-disubstituted product formed (yield 59%).

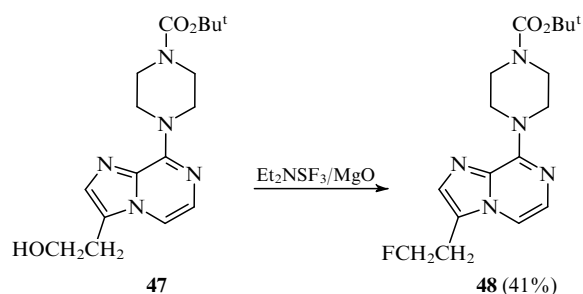
Conversely, reactions of the imidazopyrazine **21b** and 8-bromo-6-chloroimidazo[1,2-*a*]pyrazine with *N*-chlorosuccinimide lead to 3-chloro-derivatives in 72% and 90% yields, respectively.³³

Exhaustive chlorination can be achieved by using phosphorus pentachloride. For example, the imidazopyrazine **21a** is converted into 2,3,5,6,8-pentachloroimidazo[1,2-*a*]pyrazine (55%),⁸⁶ and **21i** gives 3,5,6,8-tetrachloro-derivative (10%).⁷¹

When 6,8-dichloro-3-methylimidazo[1,2-*a*]pyrazine was refluxed with NaBr/HBr in butanone,³³ selective substitution of the chlorine atom at the 8-position by a bromine atom occurs (the 6-chlorine atom being retained). The yield of 8-bromo-derivative was 67%.

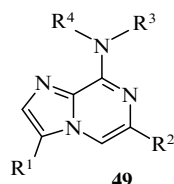
Finally, when 3-(2-hydroxyethyl)-8-(4-*tert*-butoxycarbonylpiperazino)imidazo[1,2-*a*]pyrazine **47** was treated with diethylaminosulfur trifluoride in the presence of magnesium oxide as a

catalyst, the hydroxy-group was replaced by a fluorine atom,³⁴ which resulted in the synthesis of fluoro-derivative **48**.



As noted above, substitution of halogen atoms is a convenient method for introducing other substituents into the imidazopyrazine nucleus. This substitution is used most frequently to introduce amino-groups.

This reaction is fairly selective; when the nucleus contains halogen atoms at the 3- and 8-positions or the 6- and 8-positions, substitution involves only the 8-halogen atom to give compounds **49a-i** (Table 5).^{33, 34, 65, 87, 135, 137}

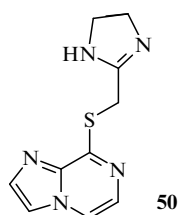


The NH group in the piperazine ring is protected by introducing a *tert*-butoxycarbonyl group (compounds **47**, **48** and **49l, m**).³⁴

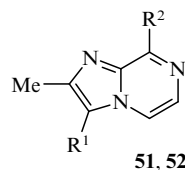
Table 5. Imidazopyrazines **49a-m** obtained by substitution of amino-groups for the bromine atom at the 8-position.

49	R¹	R²	R³	R⁴	Ref.
a	Br	H	H	H	87
b	Br	H	H	Me	87
c	Br	H	H	Et	87
d	H	Br	H	H	87
e	H	Br	H	Me	87
f	H	Br	H	Et	87
g	H	Br	-(CH ₂) ₂ O(CH ₂) ₂ -		87
h	H	Cl	-(CH ₂) ₂ NH(CH ₂) ₂ -		65
i	Me	Cl	-(CH ₂) ₂ NH(CH ₂) ₂ -		33
j	H	Ph	-(CH ₂) ₂ NH(CH ₂) ₂ -		33
k	H	H	-(CH ₂) ₂ NMe(CH ₂) ₂ -		34
l	H	Me	-(CH ₂) ₂ N(CO ₂ Bu ^t)(CH ₂) ₂ -		34
m	Me	Me	-(CH ₂) ₂ N(CO ₂ Bu ^t)(CH ₂) ₂ -		34

Substitution of the halogen atoms has also been used in the synthesis of a series of 8-(2-imidazolylmethoxy)-, 8-(2-imidazolylmethylthio)- and 8-(2-imidazolylmethylamino)imidazo[1,2-*a*]pyrazines.¹³⁸ For example, treatment of 8-chloroimidazo[1,2-*a*]pyrazine with thiourea followed by hydrolysis of the product with potassium carbonate has given a 8-sulfanyl-derivative, which has been converted into imidazopyrazine **50** by the reaction with sodium methoxide and 2-chloromethyl-2-imidazoline.



Treatment of the 8-chloroimidazopyrazines **21e** and **21s** with Grignard reagent (phenethylmagnesium bromide) and copper(I) phenylacetylide has given the corresponding substituted imidazopyrazines **51** and **52**.^{78, 82}

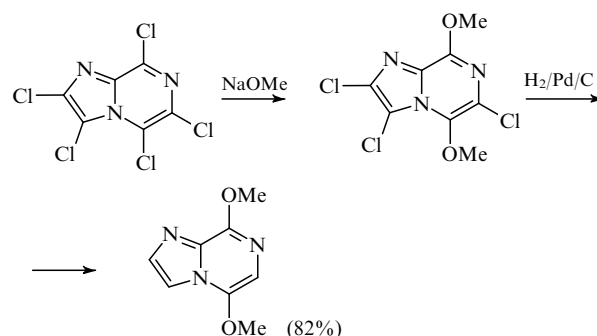


51: R¹ = H; R² = CH₂CH₂Ph (62%);
52: R¹ = Me; R² = C≡CPh (68%).

The ethynyl group in the compound **52** can be reduced to the vinyl group (yield 41%) by hydrogenation in the presence of the Lindlar catalyst (lead-poisoned 5% Pd/CaCO₃).⁸²

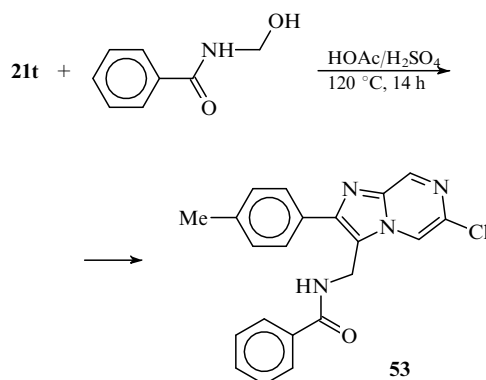
Substitution of the chlorine and bromine atoms by methoxy-groups can be accomplished by treatment with sodium methoxide.^{86, 136} In the case of polyhaloimidazopyrazines, the halogen atoms at the 5- and 8-positions are replaced predominantly. It was not specified in this study, which of these two positions is preferentially attacked. The remaining halogen atoms can be removed by hydrogenation in the presence of Pd/C (Scheme 10).^{86, 136}

Scheme 10

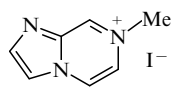


However, in the case of 6,8-dibromoimidazo[1,2-*a*]pyrazine, only the 8-bromine atom is substituted, whereas the 6-bromine atom remains unaffected, and the reaction yields 6-bromo-8-methoxyimidazo[1,2-*a*]pyrazine.¹³⁶

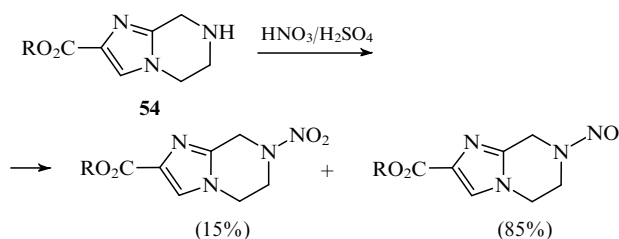
Other substituents can also be introduced in the imidazopyrazine nucleus. For example, when unsubstituted imidazo[1,2-*a*]pyrazine **21a**¹³⁹ and 6-bromo-8-methoxyimidazo[1,2-*a*]pyrazine⁸⁷ react with formaldehyde, regioselective hydroxymethylation in the 3-position occurs. Nitrosation of 8-(benzyloxy)-2-methylimidazo[1,2-*a*]pyrazine (**21o**) with sodium nitrite followed by reduction of the nitroso-derivative with metallic zinc resulted in the introduction of an amino-group in the 3-position of this compound.⁷⁸ Synthesis of 3-benzamidomethyl derivative **53** has been reported.⁸³



Alkylation of the pyrazine nitrogen atom has also been used for synthetic purposes. Thus treatment of the compound **21a** with MeI (methanol, 5 days, room temperature) affords imidazopyrazinium salt in 11% yield.¹³⁶

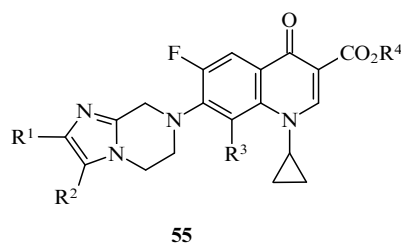


Nitrosation and nitration of tetrahydroimidazopyrazines **54** also involves the N(7) atom,⁷⁰ and treatment with HNO₃/H₂SO₄ leads to a mixture of 7-nitro- and 7-nitroso-derivatives.



R = Me, Et.

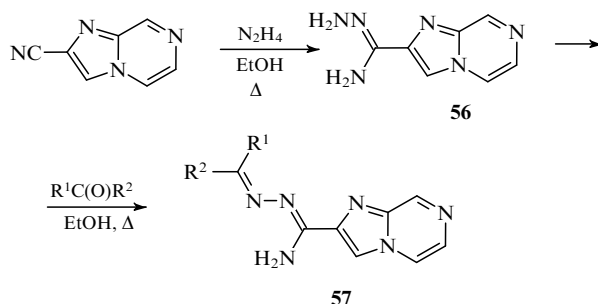
Similarly, a series of 7-substituted derivatives **55** have been obtained by arylation of tetrahydroimidazopyrazines **54**.^{140–142}



R¹, R² = H, Alk, Ph; R³ = Hal; R⁴ = H, Alk.

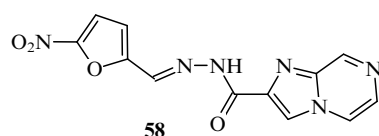
The esters **21i,k,l** can be hydrolysed to the corresponding carboxylic acids or converted into the corresponding amides by reaction with NH₄OH (or into hydrazides by reaction with N₂H₄) and then into nitriles by treatment with POCl₃.⁷¹ The latter were successively converted into amidrazones **56** and **57** according to Scheme 11.^{71, 143}

Scheme 11



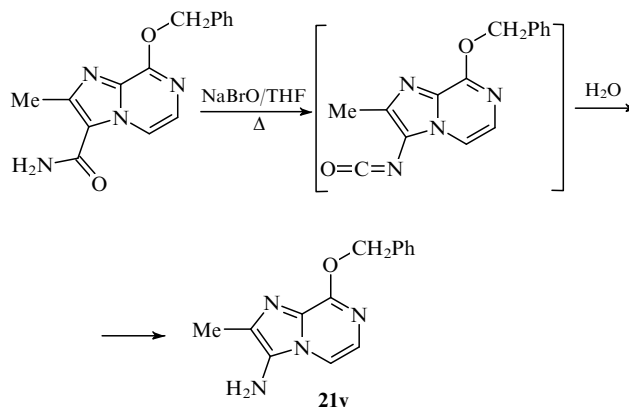
R¹ = H, Me; R² = Me, Ac, Ph, *p*-O₂NC₆H₄, anisyl, furyl;
R¹ R² = -(CH₂)₅-.

Further functionalisation of the hydrazide has resulted in the synthesis of nitrofur derivative **58**.¹⁴⁴



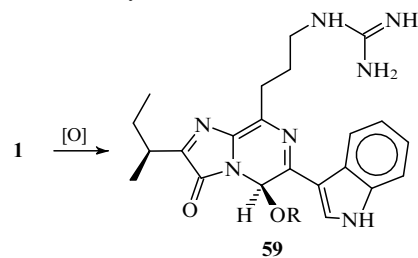
It is possible to convert amides into the corresponding amines as has been demonstrated by the synthesis of the imidazopyrazine **21y** (Scheme 12).¹⁴⁵

Scheme 12



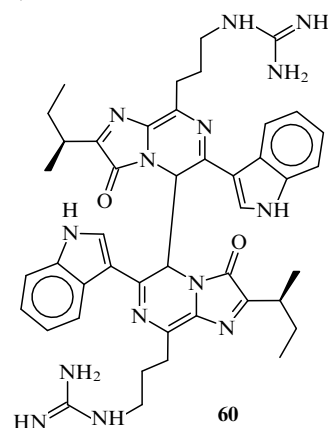
Substitution of the 2-chloromethyl groups in the imidazopyrazine nucleus by hydroxymethyl groups (refluxing in an aqueous solution of Na₂CO₃)⁷¹ and substitution of 2-benzoyloxymethyl groups by hydroxyethyl groups (refluxing in a solution of MeNH₂ in aqueous methanol)³⁴ have been reported. 8-Methoxy groups are replaced by methylamino-groups on refluxing in an aqueous solution of MeNH₂.⁸⁷ Imidazopyrazine **21z** [R¹ = R³ = R⁴ = R⁵ = H; R² = CH(OH)Me] is oxidised by manganese(IV) oxide to give the corresponding ketone.⁹⁵

Among the reactions involving natural imidazopyrazine luciferins and their analogues, oxidation of the luciferin **1** to luciferyls **59** is noteworthy.¹⁴⁶

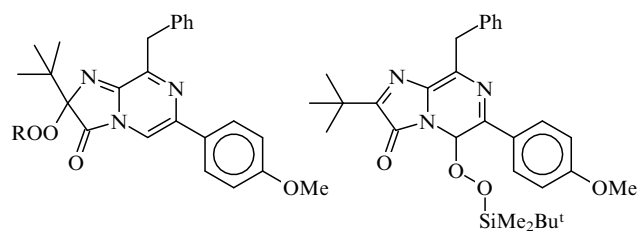


R = H, Me, Prⁱ, Buⁿ.

When alcohols are used as solvents and PbO₂ is used as the oxidising agent, the reaction yields luciferyl ethers **59** (R = Alk). The corresponding alcohol **59** (R = H) can be obtained by oxidation under milder conditions: with diphenylpicrylhydrazyl as the oxidizing agent and in aprotic media (for example, DMF). In the latter case, dimeric biluciferyl **60** is formed as an intermediate product. This compound can be isolated when the luciferin **1** is oxidised with K₃[Fe(CN)₆].¹⁴⁷ Reduction of the compounds **59** (R = H) and **60** with Na₂S₂O₄ recovers the initial luciferin **1**.^{146, 147}



Introduction and/or modification of side substituents in the existing imidazopyrazine nucleus has been used in the synthesis of coelenterazine analogues. For example, radical oxidation of the *O*-methyl derivative of the compound **14a** involving the 2-position^{148,149} or the 5-position¹⁵⁰ gives rise to the following peroxide derivatives:



R = Me₃C, Me₃Si.

The 4'-methoxy-groups themselves in the *O*-methyl derivative of the compound **14a** and other compounds of this type often play only a protective role and can be subsequently removed by treatment with pyridine hydrochloride at 210 °C for 2 h under an argon atmosphere.⁴⁸ In addition, free phenolic groups can be protected by acetylation with acetic anhydride in the presence of catalytic amounts of H₂SO₄.¹⁵¹ This approach has been used in the synthesis of the β-D-glucuronopyranoside of coelenterazine **61**,²³ which exhibits bioluminescent properties (Scheme 13).

Treatment of coelenterazine with acetic anhydride in the presence of catalytic amounts of concentrated sulfuric acid at room temperature has led to its tri-*O*-acetyl derivative (yield 86%).⁶⁰ The subsequent selective hydrolysis and treatment with the Py · SO₃ complex in pyridine at room temperature resulted in the substitution of the enol residue at the imidazole ring by a sulfate group. The two remaining acetate groups were selectively eliminated. These reactions resulted in the synthesis of coelenterazine enol monosulfate.⁶⁰

IV. Reactions

The methods for the synthesis of imidazopyrazines involving introduction or modification of side groups, considered in the previous Section (III.4), give a good idea of the reactions known for imidazopyrazines, despite the fact that the studies considered have been devoted just to the development of synthetic procedures. The reactions that have received no practical use have not been studied systematically, except for the study of mechanisms of luminescence of luciferins (see below).

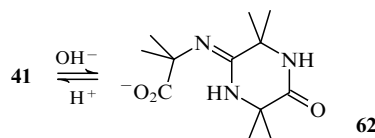
The reaction of the imidazopyrazine **21a** with hydrazine leads to a mixture of 2-methylimidazole and 1-ethyl-2-methylimidazole in a ratio of 5:4.⁶³ It was thus suggested that the reaction mechanism includes the attack by hydrazine either at the 5-position or at the 8-position of the imidazopyrazine molecule (Scheme 14).

Phenyllithium reacts with the compound **21a** yielding 8-phenyl-substituted derivative **27** and 5,6-dihydro-8-phenylimidazo[1,2-*a*]pyrazine in a ratio of 1:3.¹⁵² Methylolithium reacts with the imidazopyrazine **21a** in a similar way.¹⁵³

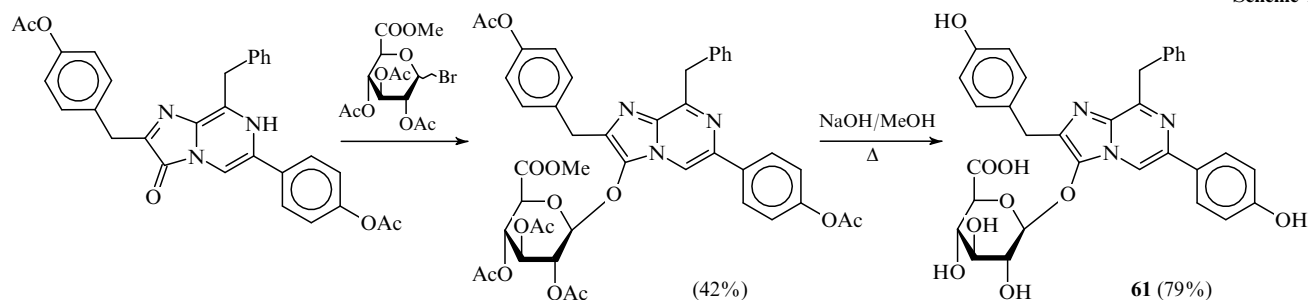
It has been found that, unlike imidazo[1,2-*a*]pyrimidine and imidazo[1,2-*c*]pyrimidine, 2- and 3-methylimidazo[1,2-*a*]pyrazines do not undergo the Dimroth rearrangement.^{61,154}

Catalytic hydrogenation of the bis-imidazopyrazine **37** leads to *N*-(2-aminoethyl)pyrazine.¹⁰⁹

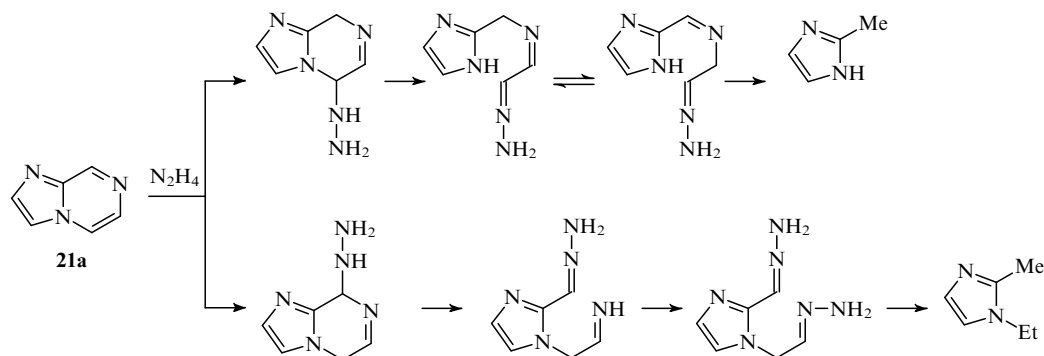
The behaviour of the imidazopyrazine **41** during hydrolysis has been studied.¹¹⁵ Although the molecule of this compound incorporates amino-acid structural fragments and, hence, it resembles somewhat cyclic peptides, the compound **41** proved to be much more resistant to hydrolysis than peptides. For example, hydrolysis of **41** in alkaline aqueous methanol stops at the stage of formation of 'amidino-acid' salt **62**, which is readily converted into the initial compound **41** in acid or even in neutral solutions.



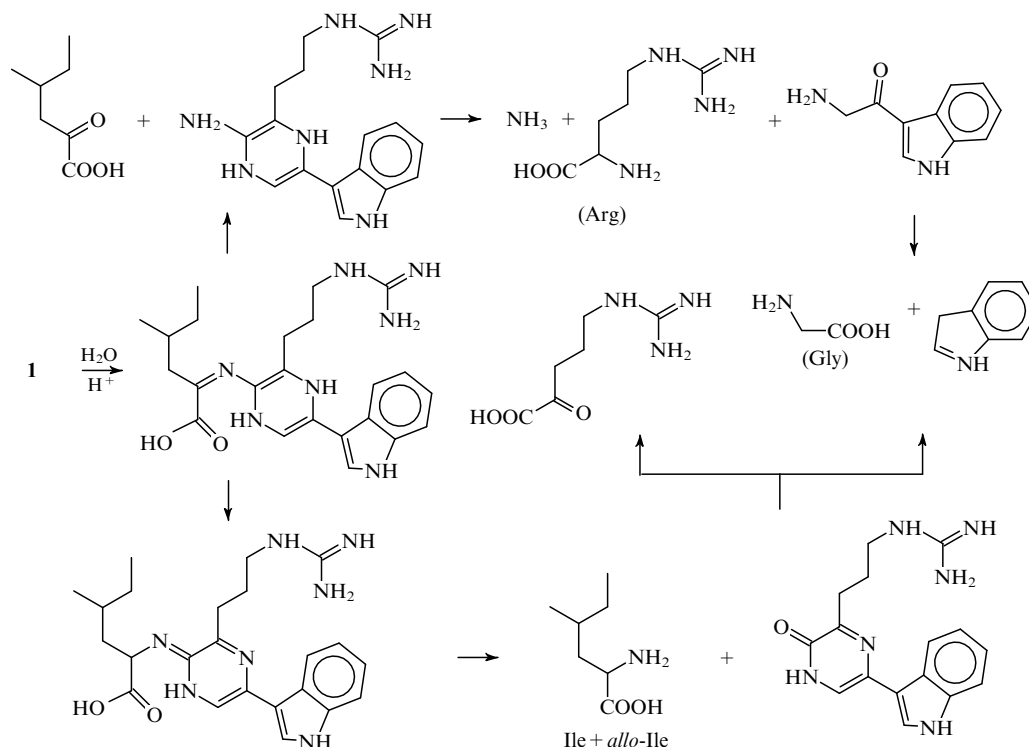
Scheme 13



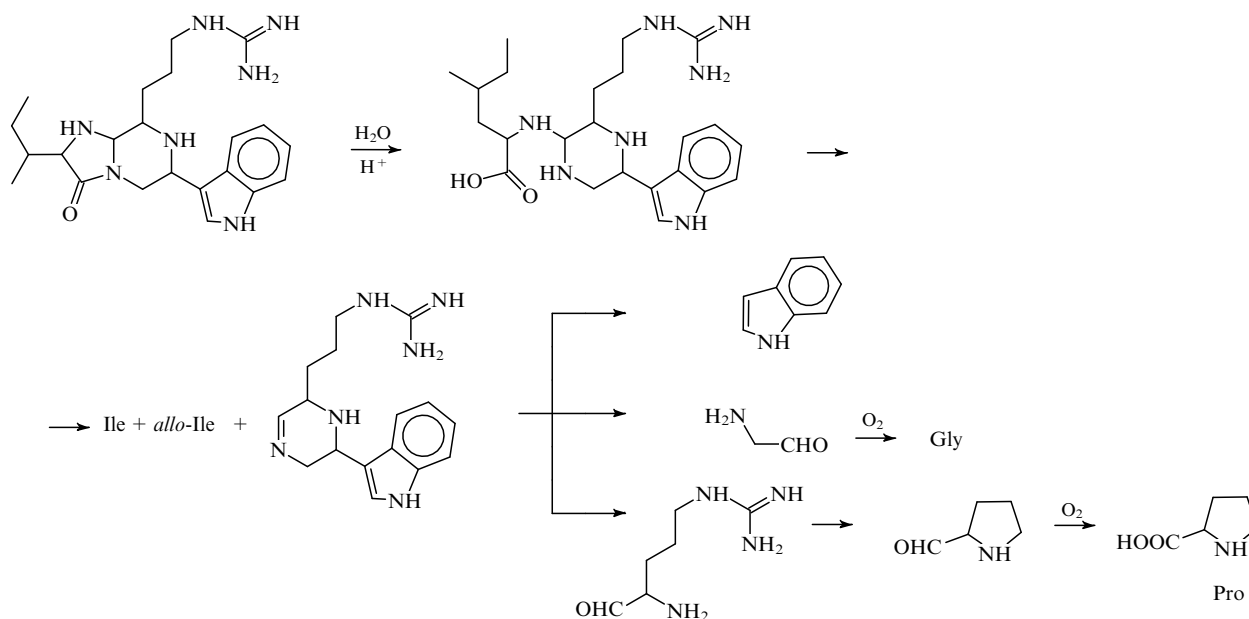
Scheme 14



Scheme 15



Scheme 16



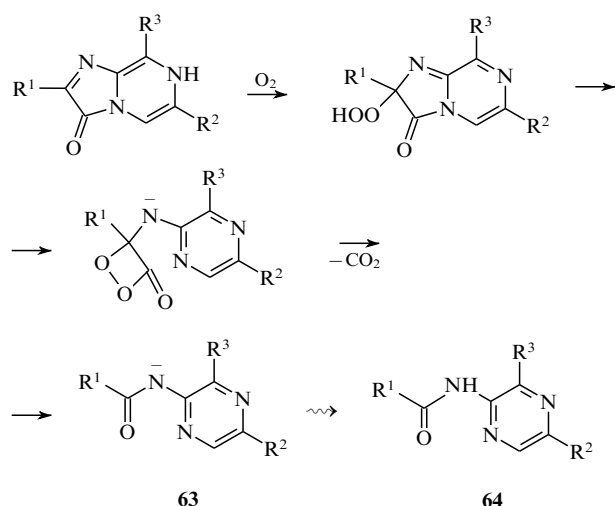
In order to determine the structure of the luciferin **1**, products of its hydrolysis as well as those of hydrolysis of its 1,2,5,6,7,8-hexahydro-analogue (6 M HCl at 100 °C) have been analysed.^{8,9} The amino acids Gly, Arg, Ile and *allo*-Ile and γ -guanidino- α -oxobutanoic acid were detected in hydrolysates obtained from the luciferin **1**, while hydrolysates obtained from its hexahydro-analogue contained Gly, Pro, Ile and *allo*-Ile. Based on these results, the researchers proposed mechanisms for the hydrolysis of these compounds (Schemes 15 and 16).

The most complex problem in the investigation of reactions of imidazopyrazines was to elucidate the mechanism of luminescence (bio- and chemiluminescence in various molecular systems) of luciferins and their analogues. Studies along these lines were started more than 30 years ago. The results of these studies have

been reported in a vast number of papers and reviews.^{2–4, 16, 17, 45, 47–49, 51–53, 58, 59, 133, 148, 155–189} However, at present, specialists admit that the molecular mechanism is ‘still unclear’, and the problem is discussed within the framework of a ‘working hypothesis’ (see, for example, Ref. 148).

Nevertheless, based on the accumulated data, it was concluded that the chemiluminescence of the luciferin **1**, coelenterazine and their synthetic analogues containing a 3,7-dihydroimidazo[1,2-*a*]pyrazin-3-one structural fragment (the compounds **14**, **16–18**, **45** and **46**) obeys identical rules, and its simplified mechanism is presented below (Scheme 17):^{47, 58 148, 158, 161, 167}

Scheme 17



Light is emitted by the excited dianion **63** of oxyluciferin **64** (or of coelenteramid in the case of luminescence of coelenterazine), and the latter can be isolated in a pure state after the completion of the reaction. Chemiluminescence is observed in aprotic solvents (1,2-dimethoxyethane, acetonitrile, dichloromethane, DMSO, etc.) in the presence of bases. For bioluminescence of the luciferin **1** and its analogues, the presence of luciferase is needed. As has already been noted, coelenterazin is a prosthetic group of the calcium-binding protein aequorin, bioluminescence of which has been induced by introduction of calcium ions.^{16, 17, 49, 148}

The efficiency of chemiluminescence has been investigated and a rate constant for the reaction of an analogue of the luciferin **1** with peroxide anion and single oxygen in various molecular systems have been determined in some other studies.^{19–20, 1}

V. Spectral and some other properties

Publications dealing with the synthesis and reaction of imidazopyrazines like many traditional studies in the organic chemistry, include characterization of compounds obtained by NMR, UV and IR spectroscopy, MS and X-ray diffraction. Therefore, the reader is interested in this topic can find the information in the original publications.

However, some papers, especially devoted to spectra and structural studies of individual imidazopyrazines, have also been published. For example, among the studies dealing with the spectra (mostly luminescent properties) of luciferin, considered in the previous Section, Refs 16 and 16 should be distinguished; in these studies, tautomerism of natural luciferin and their analogues was studied in detail by NMR and UV spectroscopy. Mass spectrometry plays a significant role in elucidating the mechanism of luminescence of these compounds.^{9, 13, 176}

Some physical methods of analysis (UV, IR and NMR spectroscopy and MS) have been invoked to confirm the unusual structure of the azacyclo **44**.^{11–9, 128} In addition, papers especially devoted to X-ray diffraction studies of these compounds have been published.^{202–203} The structure of 1,2,3,5,6, *a*-hexahydro-8, 8-diphenylimidazo[1,2-*a*]pyrazine **35** has also been characterized by X-ray diffraction data.¹⁰⁷

The use of NMR (usually ¹H NMR) spectroscopy to investigate various aspects of the structure and reactivity of imidazopyrazines has been reported.^{61, 86, 88, 89, 204–208} The structural conditions for the Dimroth rearrangement have been determined for a series of imidazopyrazines (including the compounds **21e**, **f** which do not enter into this rearrangement).⁶¹ The site of protonation and tautomeric equilibrium for a number of compounds of the type **18** and **21** have been studied by ¹H NMR,^{88, 89} ¹³C NMR,^{205, 206} and ¹⁵N NMR²⁰⁵ spectroscopy. A correlation between the position of the ring nitrogen atoms in

various azoloazines (including the imidazopyrazine **21a**) and the corresponding chemical shift has been established.²⁰⁷ Yet another application of NMR spectroscopy (¹H and ¹⁵N) has been the determination of the site of nucleophilic substitution in the molecule of the imidazopyrazines **21**.^{86, 204–208}

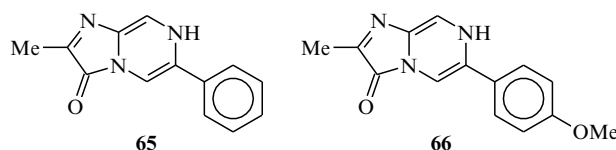
The site of protonation of the molecule **21a** have been determined using magnetic circular dichroism²⁰⁹ and UV spectroscopy.³⁸ The electronic structure of this compound (among other fused 5- and 6-membered aza-heterocycles) has been discussed based on the data of UV spectroscopy.^{210–211}

VI. Applications

It is not an exaggeration to say that luciferin in coelenterazin **2** and their synthetic analogue possess the most unusual properties among all known imidazo[1,2-*a*]pyrazines. Their ability to luminesce under the action of oxidants and the influence of various factors on this process permitted the development of a number of fairly specific analytical procedures.

In particular, luciferin and its synthetic analogue have been used for chemiluminescent determination of peroxide (including organic),^{212–219} oxygen,²²⁰ oxidase,²²¹ peroxidase,²²² glucosidase,²²³ galactosidase²²⁴ and ATP;²²⁵ for investigations of the reaction of amino acid and related compounds with peroxide anions²²⁶ and of the formation of peroxide anions in human blood cells;^{22–229} in other cytological studies;^{23–234} for chemiluminescent immunoassays²³⁵ and for the development of sensors based on immobilized enzymes.^{235–236}

Compounds **65** and **66** denoted by the abbreviations CLA and MCLA are analogues of luciferin. In these are used most frequently.



It has been noted (see for example, Refs 45 and 237) that MCLA is more effective than CLA for detecting oxidant formed during enzymic reactions. This is due to a higher quantum yield in the former case and also to the fact that the maximum of its luminescence is shifted to the visible region to a greater extent (for CLA, λ_{max} is 45 nm⁵⁸ and for MCLA, it is 46 nm⁴⁵).

It has been reported that the introduction of one of the analogues of Cypridin aluciferin in a tissue decreases the probability of fibrillation induced by ischemia and reperfusion.²³⁸

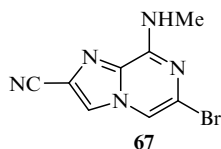
The main field of application of coelenterazin and its synthetic analogue is luminescent determination of calcium ions. As noted above, bioluminescent properties are inherent in the protein aequorin, in which the coelenterazin molecule acts as a prosthetic group. Bioluminescence is observed only in the presence of calcium ions,^{1, 61, 79, 50, 148, 239, 240} while in the absence of these ions the protein is very stable.

The method of investigation of the dynamics of calcium ions in living tissue is based on the formation of recombinant aequorin from coelenterazin or its analogue and the protein apoaequorin produced in the cells.^{241, 242} In a comparative study of the natural coelenterazin **2** and its synthetic analogues, it has been found that the recombination of aequorin occurs most rapidly when natural coelenterazin is used.^{243–244}

In the absence of protein, non-bound coelenterazin can be used as a luminescent probe for peroxide ions²⁴⁵ and also for investigation of translation in cell-free systems.²⁴⁶

The main field of application of synthetic imidazopyrazines having no natural analogue is pharmacology. Some compounds of this class are capable of depressing the secretion of gastric juice; therefore, they can be used as anti-ulcer drugs.^{78, 79, 82, 145, 247–252} Among the imidazopyrazines mentioned in this review, the derivative **21y**, known under the code name SCH 32651, is the most active.^{78, 145, 247–249}

Another type of pharmacological activity found for some representatives of this class of compound is the ability to relax smooth muscles.^{71, 87, 135, 253–258} For example, it has been found that^{71, 87} the imidazopyrazines **21k–m**, **49a–g** and some others possess more pronounced bronchospasmolytic properties than theophylline; as a rule, the activity of these compounds increases when bromine atoms are introduced in their molecules as substituents. 6-Bromo-8-methylaminoimidazo[1,2-*a*]pyrazine-2-carbonitrile **67** referred to as SCA 40 has been chosen for a systematic pharmacological assay.^{254–258}



Cardiotonic properties (i.e. the ability to enhance systoles) have been discovered for derivatives containing methoxyphenyl and other aromatic substituents in the 2-position of the heterocyclic nucleus,^{72–76, 77, 80, 259–261} for example, for the imidazopyrazines **21p–r**.

More complex compounds such as **55**,^{140–142} **58**¹⁴⁴ as well as peneme^{262, 263} and cepeme²⁶⁴ antibiotics with imidazopyrazine substituents have been proposed as antibacterials.

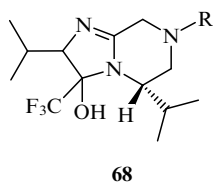
Some imidazo[1,2-*a*]pyrazine-2-carboxylic acids, imidazo[1,2-*a*]pyrazine-3-carboxylic acids^{62, 64, 73, 84, 265} and the adenosine analogue **7**³⁷ exhibit anti-inflammatory activity. Some carboxyl-containing derivatives have been found to possess analgesic properties.

Imidazopyrazine analogues of nucleosides can prove to be effective antiviral preparations and immunomodulators.^{36, 37, 266} For example, the compound **7** inhibited AIDS virus proliferation in T cells by 70%.³⁶

It has been proposed to use the piperazino-derivatives **49h–k** as appetite-suppressing agents; as antidepressants; as antihypertensive, analgesic and antiarrhythmic preparations and in the fight against smoking.^{33, 65, 267} 8-Piperazinoimidazo[1,2-*a*]pyrazine has exhibited hypoglycemic activity.^{34, 268}

Ethyl 2,3,5,6,7,8-hexahydroimidazo[1,2-*a*]pyrazine-7-carboxylate has proved to be useful in the therapy of schizophrenia.⁹³

The trifluoromethyl-substituted imidazo[1,2-*a*]pyrazines **68** have been found to be effective inhibitors of elastase and are considered as possible drugs for treatment of lung emphysema and related diseases.^{269, 270}



R = 3,4-(MeO)₂C₆H₃CH₂CH₂, 2-indanyl, cyclooctyl.

Derivatives of oxoquinoline- and oxonaphthyridinecarboxylic acids containing imidazopyrazine substituents have been patented as preparations for the treatment of acute myocardial infarction, osteoporosis and tumours.²⁷¹

There are only few examples, where synthetic imidazopyrazines have been used for other than pharmacological purposes. To the best of our knowledge, only a method for extraction of metal ions (Mo, Cr, Pb, Au, Ag, Pt, U, *etc.*) using the compound **36**¹⁰⁸ has been patented and materials for colour photography based on 5-hydroxyimidazo[1,2-*a*]pyrazines have been developed.^{272, 273}

VII. Conclusion

Our analysis of the published data indicates that considerable progress has been achieved during the four decades of studies dealing with imidazo[1,2-*a*]pyrazines.

A number of methods for the synthesis of this class of compound have been developed. These methods permit preparation of products with different degrees of saturation of the imidazopyrazine nucleus and with side substituents of various natures. The approach based on the construction of the imidazole ring when the pyrazine fragment is already present in the molecule is used most frequently. Among the reagents used for these purpose, the best results have been generally achieved when pyrazines have been involved in condensation with α -halocarbonyl compounds. Glyoxals proved to be indispensable in the synthesis of natural luciferins and model compounds.

The synthesis of 'azacyclols' presented a separate task. It was accomplished using reagents and procedures adapted from peptide chemistry. This task was even more complicated due to the presence of chiral centres in the amino-acid residues — structural fragments of 'azacyclols' — and to the lability of the C(8a)OH group.

The current views on reactions of imidazopyrazines are mostly based on the data accumulated in the synthesis of new compounds of this class by introduction of side substituents into the heterocyclic ring and their subsequent modification. Systematic studies on the reactivity of imidazopyrazines have scarcely been carried out, except for the studies dealing with the structure of luciferins and the mechanism of their luminescence.

Studies of the spectroscopic properties and characteristic features of the electronic and spatial structures of some imidazo[1,2-*a*]pyrazines are not significant by themselves; as a rule, they only supplement synthetic studies by a standard set of analytical data for new compounds. Works, in which the attention is focused on these aspects (for example, studies on the tautomerism, sites of protonation and reactivity, confirmation of an unusual structure, *etc.*), are few in number.

About a quarter of all publications (including patents) on imidazopyrazines are devoted to their use or mention their possible applications (mostly in analytical chemistry, biochemistry and pharmacology).

Analysis of the published data makes it possible to distinguish some specific features in the development of this branch of the chemistry of heterocyclic compounds. As has been mentioned in the Introduction, the studies devoted to the synthesis and studies of imidazopyrazines follow three absolutely separate lines of research:

- (1) natural luciferins and their analogues;
- (2) 'cyclols' and other derivatives of cyclic tripeptides;
- (3) imidazopyrazines having no natural analogues.

The studies along the first line were actually initiated by the discovery of *Cypridina* luciferin and coelenterazine in living organisms. Although these are only two representatives of the vast class of imidazopyrazines, their properties are so interesting that publications dealing with the synthesis of their analogues and with the conclusive determination of the mechanism of their luminescence are still appearing in the literature. These studies occupy an important place among those dealing with the chemistry of imidazopyrazines.

The fate of the second line of research is somewhat unexpected and, from the author's viewpoint, difficult to explain. The first studies on the synthesis of 'azacyclols' were published in the early 70s, while the last ones appeared in the middle 80s. Despite the fact that these compounds are extremely interesting, this line is at a deadlock. Its development stopped about ten years ago and did not result even in recommendations on practical applications of azacyclols. According to the personal viewpoint of the author, development of more general and convenient methods for the synthesis of these compounds (including, for example, fluorinated derivatives) and appropriate pharmacological assays would not

only fill the gap in the purely practical aspect but also markedly contribute to peptide chemistry. The possibility of preparing other imidazopyrazine analogues of cyclic tripeptides directly from amino acids also deserves more attention.

As regards the chemistry of synthetic imidazopyrazines having no natural analogues, its development follows the traditional route for the majority of classes of organic compounds. Since many of the compounds synthesised exhibited valuable pharmacological properties, the search for new derivatives of this type is being carried out. Although it seems that pharmacology does not encompass all the possible applications of these compounds, other practical aspects are scantily presented in the scientific literature.

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Phosphorylated allenes: structure and interaction with electrophiles

I V Alabugin, V K Brel

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Abstract. Data on the structures of phosphorylated allenes (PA) and their reactions with electrophiles are surveyed for the first time. It is shown that the influence of intramolecular interactions on the reactivity of the unsaturated centres is reflected in the selectivity of the reactions of PA with electrophiles. Depending on the nature of the reactants and the structure of the PA, various reaction mechanisms may operate. The bibliography includes 163 references.

I. Introduction

The unusual system comprising interlinked unsaturated centres, differing in properties and reactivity, in molecules of phosphorylated allenes (PA) as well as the ready availability of these compounds and the wide variety of chemical reactions based on them have long attracted the attention of chemists (see, for example, Refs 1–4). Vigorous studies on PA are also being continued at the present time. The results obtained in recent years have appreciably altered and amplified the general ideas concerning the compounds of this class. Firstly, the range of synthetic reactions based on PA has expanded significantly and it became necessary to refine the concept of their reactivity. Secondly, it was in fact in recent years that the structures of certain PA were first investigated by X-ray diffraction methods (in the case of crystalline substances) and by gas electron diffraction (in the gas phase). In addition, the quantum-chemical calculations which have been carried out (both by semiempirical and *ab initio* methods) together with photoelectron spectroscopic data made it possible to characterise fairly reliably for the first time the electronic structure of PA. In connection with the growing interest in the synthesis of promising physiologically active substances^{5–17} from PA, a systematic treatment and combined analysis of the experimental data accumulated were required. The present review surveys the new data on the structure of PA and their interaction with electrophiles.

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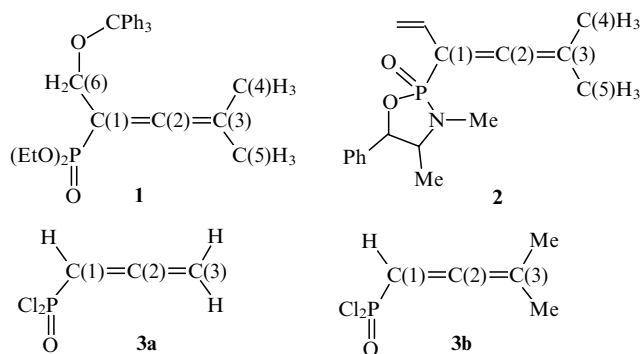
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II. Characteristic features of the structure of phosphorylated allenes

The mutual influence of three fragments — two mutually orthogonal double bonds and the phosphoryl group — in PA molecules can be exerted both *via* bonds and through space^{18–20} and can alter the properties and reactivity of these isolated fragments.

Up to the beginning of the 1990s, the structures of PA had not been investigated and studies^{21,22} on the X-ray diffraction of the allenic phosphonate **1** and the allenic 1,3,2-oxazaphospholidine **2** as well as the report²³ concerning the investigation of the dichlorides of allenylphosphonic acid **3a** and 3-methylbuta-1,2-dienylphosphonic acid **3b** by gas electron diffraction (GE) were published only a few years ago. The geometrical parameters of the principal fragments of molecules of compounds **1–3a,b** are presented in Table 1.



The allene fragment in PA molecules is linear and has an orthogonal configuration of the substituents at the C(1) and C(3) atoms. The C(1)=C(2) bond is somewhat longer than the double bond remote from the phosphorus atom. The lengths of both bonds are close to the value 1.3129(9) Å obtained²⁴ for propadiene $\text{CH}_2=\text{C}=\text{CH}_2$.

The lengths of the P–Cl bonds in the molecules of the dichlorides **3a,b** [2.011(1) and 2.024(2) Å respectively] are close to the values found for vinylphosphonic dichloride $\text{CH}_2=\text{CH}-\text{P}(\text{O})\text{Cl}_2$ [2.016(4) Å]²⁵ and methylphosphonic dichloride $\text{MeP}(\text{O})\text{Cl}_2$ (2.011–2.013 Å)²⁶ and are somewhat greater compared with the analogous bonds in the POCl_3 molecule [1.992(3) Å]. The P=O (1.453 Å) and P–O (1.566–1.574 Å) bonds in the molecule of the allene **1** have lengths almost identical with the statistical average values for the $(\text{XO})_2\text{P}(\text{O})-\text{C}$ fragments 1.457(9) Å for P=O and 1.571(13) Å for P–O.²⁷

In the molecules of the allenes **1** and **3a**, which are predominantly (100% and 72% respectively) in the *s-cis*-conformation

Table 1. The bond lengths (d) and O=P–C=C torsional angles (φ) in the molecules of the PA **1–3a,b**.

Com- pound	Met- hod	$d/\text{\AA}$				φ/deg
		C(1)–C(2)	C(2)–C(3)	C(1)–P	P=O	
1	XRD	1.316(3)	1.308(3)	1.787(2)	1.453(2)	0
2	XRD	1.311(3)	1.307(4)	1.812(2)	1.465(2)	130
3a	GE	1.318(4)	1.318(4)	1.795(3)	1.461(3)	0 (72.1%) ^a 123 (27.9%) ^a
3b	GE	1.307(7)	1.307(7)	1.804(9)	1.451(7)	0 (51.6%) ^a 109.1 (48.4%) ^a

^a The fraction of the corresponding conformation.

(the O=P–C=C torsional angle is $\varphi = 0^\circ$), the P–C(1) bond is somewhat shorter compared with the statistical average length of the P–C(sp^2) bond, which is 1.81 Å^{26,28–30} (1.817–1.822 Å for the dichloride of vinylphosphonic acid); in the case of the allene **3b** (51.6% of the *s-cis*-conformation), this effect is weaker; in the molecule of compound **2**, where the O(1)=P–C(1)=C(6) fragment has the anticlinal conformation, the P–C(1) bond length is close to the standard value. This suggests either a comparatively lower degree of conjugation in the molecules of *s-cis*-PA or the occurrence of a different, specific to allenylphosphonates, intramolecular interaction in the case of the *s-cis*-conformation. This question will be considered below; we shall only note that the interaction through space of the 3d orbitals of the P atom with the π -system of the allyl double bond, mentioned previously, is impossible for PA because of considerations relating to the molecular geometry.³¹

The conformational composition of the PA has been investigated with the aid of vibrational spectroscopy (IR and Raman),^{32–35} the dipole moment method,^{36,37} the Kerr effect,³⁶ and electron diffraction in the gas phase.²³ The results of all the investigations show that the principal conformation relative to the C–P bond is cisoid, characterised by the coplanar disposition of the O=P–C=C fragment ($\varphi \approx 0^\circ$). The fraction of this conformation varies as follows: 72% in the gas phase²³ and 70% in solution³⁷ for the allene **3a**, 51.6% in the gas phase²³ for the phosphonic dichloride **3b**, and 100% in the crystalline state for compounds **1** and **3a,b** and a number of other allenes^{21,37} (with the exception of compound **2**).²² Our calculation of the dependence of the total energy of the allene **3a** molecule on the O=P–C(1)=C(2) angle by the PM3 method demonstrated the presence of two minima — a deeper minimum corresponding to the *cis*-conformation ($\varphi = 0^\circ$) and a shallow minimum at 180° . The rotational barrier is $< 2 \text{ kcal mol}^{-1}$. These results agree with the literature data on the conformational equilibrium in the allenecarboxylic³⁸ and vinylphosphonic acids,^{35,39–41} for which the eclipsed conformation is also the most stable.

At the same time, it is essential to note that ideas concerning the geometry of the second conformer of PA (as well as vinylphosphonates) have changed in recent years. It had been postulated earlier that the minor component is characterised by planar *s-trans*-dispositions of the atoms of the O=P–C=C fragment (by analogy with acrylic acid derivatives⁴²). However, the results of recent studies on PA by gas electron diffraction²³ support a nonplanar structure of this fragment. Thus, in the case of the allenes **3a,b**, a mixture of two rotational isomers with the following angle φ corresponds to experimental data: 0° (72.1%) and 123.3° (27.9%); 0° (51.6%) and 109.1° (48.4%). The anticlinal conformation (130°) occurs also for the allene **2** in the crystalline state.

Analysis of vibrational spectra³⁵ and *ab initio* calculations^{43–45} led to similar results as regards the conformational equilibrium in the molecules of vinyl- and *trans*-propenyl-phosphonates: the second minimum corresponds to the anticlinal

conformation (the planar *s-trans*-conformation corresponds to the transition state) for rotational barriers of $\sim 3 \text{ kcal mol}^{-1}$. For the conformers of *cis*-propenyl-phosphonates, the barriers to internal rotation are much higher. The fraction of the *s-trans*-form increases with increase in the steric hindrance induced by the interaction of the phosphoryl group and the substituent in the *cis*-position and also with increase in solvent polarity.⁴⁶ The total energy minimum at $\varphi = 0^\circ$ is due to the interaction of the nonbonded atoms, while the additional minimum is caused by intramolecular charge transfer from the vinyl fragment to the phosphorus-containing group.⁴⁷

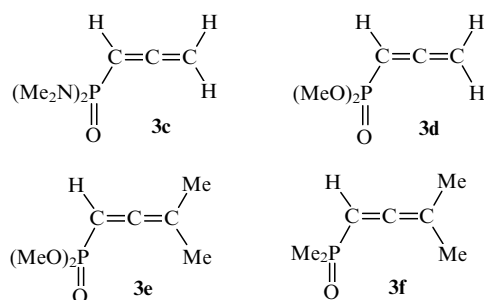
The question of the existence and extent of conjugation in PA molecules arises in connection with the nonplanar structure of the minor conformers. Since there is virtually no information about this in the literature, we shall consider briefly data on conjugation in vinylphosphonic acid derivatives, assuming that the general rules are valid also for PA. It has been noted³⁵ that the extinction coefficients of vinylphosphonates are higher than those of the homologous allylphosphonates. This indicates the presence of π -conjugation between the vinyl and phosphorus-containing fragments, but it is much weaker than, for example, in the case of acrylic acid derivatives. The absorption by propenylphosphonates is greater than by vinylphosphonates, which may be accounted for by the hyperconjugation effect of the methyl group. The negative charge on the C(1) atom of vinylphosphonic acid is higher than on the C(2) atom (Table 2). This finding was initially regarded as an argument in support of the conjugation of the double bond and the P=O group,⁴³ but it was shown later^{44,45} that in this system conjugation is manifested weakly and that the inductive effect and hyperconjugation with participation of the PO₃ fragment must be invoked in order to account for the electronic structure of vinylphosphonates. The strong π -acceptor effect of the O=PCl₂ fragment has been attributed⁴⁸ to the group π^* orbitals made up of the σ^* orbitals of the P–Cl bonds.

The structure of the PA **3a–f** has been investigated by photoelectron (PE) spectroscopy and by means of quantum-chemical

Table 2. The effective charges (q) on the carbon atoms of allene and ethene derivatives (calculated *ab initio* in terms of the 4-31 G basis set).

Compound	q/e		
	C(1)	C(2)	C(3)
H ₂ C(1)=C(2)=C(3)H ₂ 8	–0.380	–0.008	–0.380
H ₂ C(1)=C(2)=C(3)Me ₂ 7	–0.360	–0.042	–0.008
H ₂ PC(1)H=C(2)=C(3)H ₂ O 9	–0.663	0.135	–0.337
H ₂ PC(1)H=C(2)=C(3)Me O 10	–0.653	0.103	–0.008
Cl ₂ PC(1)H=C(2)=C(3)H ₂ O 3a	–0.585	0.156	–0.332
Cl ₂ PC(1)H=C(2)H ₂ O 4	–0.496	–0.214	–
Cl ₂ PC(1)H=C(2)H ₂ S	–0.432	–0.225	–

nonempirical calculations.⁴⁹ It was shown that the 4-31 G basis set is the minimal basis set for the establishment of proportionality between the calculated molecular orbital (MO) energies and the experimental ionisation potentials (IP).



According to *ab initio* calculations, the main contribution to the highest occupied MO comes from the $p\pi(\text{O})$ and the π_1 and π_2 orbitals of PA [$\pi_1(a'')$ is the orbital of the C atom closest to the P atom and $\pi_2(a')$ is the orbital of the C atom remote from the P atom; a' and a'' correspond to the symmetry and antisymmetry of these orbitals relative to the OPCC reflection plane respectively]. The ionisation energies are similar and vary as a function of the nature of the substituents at the C atom. Fig. 1 presents the correlation diagram for the ionisation potentials of a series of PA, the dichloride of vinylphosphonic acid **4**,⁴⁹ its diethyl ester **5**,⁴⁷ and the bis(dimethylamide) **6**,⁵⁰ 3-methylbuta-1,2-diene **7**, and propadiene **8**.⁵¹ The form and intensity of the bands in the PE spectra of PA permit the interpretation, to a first approximation, of the experimental IP as the ionisation energies of individual fragments of the molecule. We shall consider how the mutual influence of these fragments affects the ionisation potentials of PA.

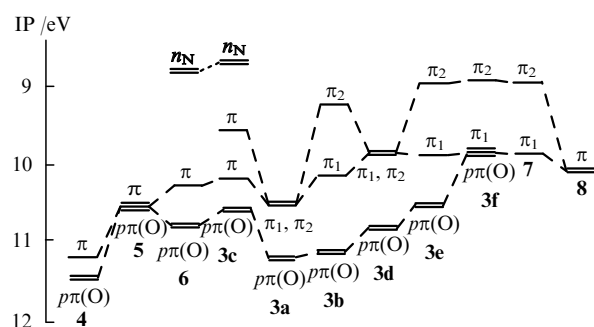


Figure 1. The correlation diagram for the ionisation potentials of the phosphorylated allenes **3a–f**, the alkenes **4–6**, 3-methylbuta-1,2-diene **7**, and propadiene **8**.

The replacement of two H atoms in the dichloride of vinylphosphonic acid by the methylene fragment increases the energy of the $\text{C}(1)=\text{C}(2)$ bond by 0.7 eV, compensating fully the decrease in the energy of the corresponding π orbital caused by the presence of the electron-accepting $\text{O}=\text{PCl}_2$ fragment (IP_1 for ethene is 10.51 eV⁵²), while the introduction of the $=\text{CMe}_2$ fragment increases the energy of the $\text{C}(1)=\text{C}(2)$ bond by 1 eV. On passing from ethene to allene, the energy of the π orbital increases by only 0.5 eV. Comparison of the data for PA with the analogous values for a series of other allenes⁵³ shows that the influence of the phosphorus-containing fragment on the π_1 bond is considerable and is largely determined by the inductive effect of the substituent. The transfer of electron density from the allene system to the phosphoryl group explains the decrease in the ionisation energy of the $p\pi(\text{O})$ orbital on passing from the dichloride of vinylphosphonic acid **4** (11.5 eV) to the dichloride of allenylphosphonic acid **3a** (11.25 eV); the ionisation energy of the $p\pi(\text{O})$ orbital of the allene **3b** disubstituted at the C(3) atom (11.14 eV) is lower still. We quote for comparison the known ionisation energies of the $p\pi(\text{O})$ orbitals for $(\text{EtO})_2\text{P}(\text{O})\text{H}$ (11.35 eV), $(\text{EtO})_2\text{P}(\text{O})\text{NEt}_2$ (11.41 eV),⁵⁴ and $\text{Cl}_2\text{P}(\text{O})\text{Me}$ (11.49 eV).⁵⁵ On the other hand, the ionisation energies of the $p\pi(\text{O})$ orbitals of diethyl vinylphosphonate **5** and the allenylphosphonic acid derivatives **3c,d**

were found to be similar, the IP of the allene **3d** being higher than that of the phosphonate **5** (10.7 and 10.6 eV respectively).

The replacement of two H atoms in the ethene molecule by the $\text{Cl}_2(\text{O})\text{P}-\text{C}=\text{C}=\text{C}$ fragment hardly influences the ionisation energy of the double bond (10.5 eV), while IP_2 of the allene **3b** is higher than the ionisation energy of the π orbital of isobutene (9.24 eV)⁵² by only 0.17 eV. Furthermore, the ionisation energy of the π orbitals of the phosphonate **3d** was found to be lower than that for the unsubstituted allene $\text{H}_2\text{C}=\text{C}=\text{CH}_2$ (10.04 eV). It had been shown earlier that the influence of the substituent on the bond of the allene system remote from it is best described within the framework of the long-range field effect, whereupon there is a correlation between the IP of monosubstituted allenes and the dipole moments of the corresponding alkenes.⁵³ It might have been expected that the introduction of a phosphorus-containing fragment would appreciably reduce the energy of the π_2 orbital and the corresponding IP of the allene **3a** would therefore be higher by 0.5 eV than the observed value (Fig. 2) For the allene **3d**, the difference between the real ionisation potential and the value expected on the basis of the inductive effect approaches 1 eV. The validity of the employment of this correlation for PA is based on the similar conformational behaviour of PA and vinylphosphonates and also on the existence of the above correlation for the π_1 orbitals. A similar albeit a weaker effect (Fig. 2) has been observed in the series of alkoxyallenes $(\text{RO})\text{HC}=\text{C}=\text{CH}_2$.⁵⁶ It can be explained by the orbital interaction of the nonbonded fragments through space.

Quantum-chemical calculations of the molecular orbital ener-

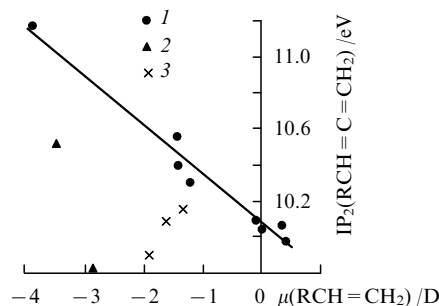


Figure 2. The correlation of group dipole moments (μ) of the substituents and the second ionisation potentials of allenes (**1**), PA (**2**), and alkoxyallenes (**3**).

gies of a series of PA by the AM1 and PM3 methods have indicated the possibility of orbital interactions specific to allene derivatives of phosphonic acids in the *s-cis*-conformation, namely, the interaction through space of the $\text{P}(\text{O})$ orbital of the oxygen atom of the $\text{O}=\text{P}$ group with the π_2 orbital in the allene system having a similar energy and symmetry (Fig. 3). The effectiveness of this interaction should increase with decrease in the difference between the energies of the π_2 and $p(\text{O})$ orbitals and hence should be manifested most strongly in the molecules of allenylphosphonic acid amides and allenylphosphine oxides. As a result of this, the *s-cis*-conformers of the latter should be additionally destabilised. The two mutually orthogonal π systems comprising the PA skeleton (the $\text{O}=\text{P}$ group may be regarded as a highly polarised triple bond⁵⁷) are analogous to the system of two triple bonds.¹⁹ For PA conformations other than the *s-cis*-form, account must be taken of the possibility of similar orbital interactions through space with participation of, for example, the lone pairs of the O atom in the POC fragment, *etc.*

Thus the mutual influence of the phosphorus-containing fragment and the double bond remote from the P atom is manifested by two mutually compensating effects, which determines the unique position of PA both in the series of other

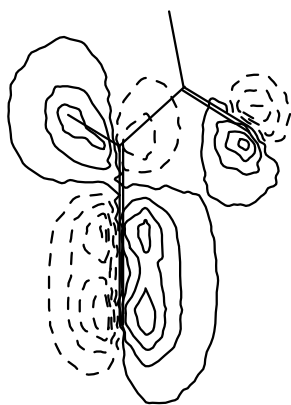


Figure 3. The highest occupied MO of the allene **3** (calculation by the PM3 method; the continuous and dashed lines correspond to different signs of the wave function).

unsaturated phosphoryl compounds and in the series of substituted allenes.

We shall consider in greater detail the changes in the allene system occurring when the substituents at the P atom are varied. The presence of the $X_2P=O$ ($X = Me, OMe, Cl$) group has little effect on the relative energies of the π_1 and π_2 orbitals: the energies of the latter in the molecules of compounds **3a** and **3d** are similar, whilst for the allenes **3b**, **3e**, and **3f** the difference between them is equal to the difference between the energies of these orbitals in the molecule of 3-methylbuta-1,2-diene **7**. The absolute energies of the π_1 and π_2 orbitals in the molecules of compounds **3e,f** and **7** are similar; in the presence of the more electron-accepting $Cl_2P=O$ group, they diminish by approximately 0.5 eV. On the other hand, in the molecule of the dimethylamide **3c** the energies of the π orbitals differ appreciably and there exists qualitative evidence supporting the assignment of IP_2 (9.56 eV) to the π_1 orbital. The presence of two methyl groups at the P atom in the phosphine oxide **3f** greatly reduces the ionisation energy for the $O=P$ group.

Table 2 presents the effective charges on the atoms of the allene fragment calculated *ab initio* in terms of the 4-31 G basis set,⁴⁹ while Table 3 presents data on the energies and compositions of the π orbitals of the two model PA **9** and **10**, the acid chloride **3a**, and the dienes **7** and **8**. Similar data have been obtained^{1,58} with the aid of the semiempirical CNDO/2 method (the *spd* basis set). The degenerate frontier orbitals of the unsubstituted allene are located predominantly on the terminal atoms. The presence of the $H_2P=O$ or $Cl_2P=O$ group in the allene molecule has little effect on the relative energies of the π orbitals, but leads to a slight delocalisation of the latter and also to a change in the polarisation of the π_1 bond. The situation changes sharply in the case of the allenes **3b,e,f** in which the degeneracy of the π orbitals is removed as a consequence of hyperconjugation with the methyl groups; the polarisation of the π_2 orbital then changes and the overall electron density on the C(3) atom is appreciably reduced.

The calculated atomic charges are satisfactorily correlated with ^{13}C NMR spectroscopic data (Table 4) and illustrate the influence of the substituents on the distribution of electron density in PA molecules. The change in the polarisation of the π_1 bond on passing from 3-methylbuta-1,2-diene to PA is manifested by a downfield shift of the C(1) signal. The presence of alkyl substituents at the C(3) atom leads to a 10–15 ppm downfield shift of its signal in the ^{13}C NMR spectrum.⁵⁹ The chemical shifts in the ^{31}P and ^1H NMR spectra of PA are in the usual range for unsaturated phosphonic acid derivatives and have been discussed in fair detail.¹

The dipole moments of PA are somewhat greater compared with those of the corresponding alkenylphosphonic and alkadienylphosphonic acid derivatives³⁶ (Table 5), the experimental values exceeding the values calculated assuming additivity. This

Table 3. The energies (E_m) and populations of the π orbitals (q_m) of a series of PA.

Compound	MO	E_m	$\pi_2[C(1)=C(2)]$		$\pi_2[C(2)=C(3)]$	
			$q_m^{z,1}$	$q_m^{z,2}$	$q_m^{x,2}$	$q_m^{x,3}$
8	ψ_1^*	4.92	0.507	0.462	—	—
	ψ_1	−10.04	0.212	0.163	—	—
	ψ_2^*	4.92	—	—	0.462	0.507
	ψ_2	−10.04	—	—	0.163	0.212
7	ψ_2^*	5.17	0.506	0.478	—	—
	ψ_2	−9.89	0.262	0.205	—	—
	ψ_1^*	4.98	—	—	0.403	0.373
	ψ_1	−9.25	—	—	0.216	0.218
9	ψ_1^*	3.42	0.359	0.504	—	—
	ψ_2	−10.72	0.186	0.120	—	—
	ψ_2^*	3.56	—	—	0.339	0.432
	ψ_1	−10.46	—	—	0.174	0.193
10	ψ_1^*	3.84	0.323	0.504	—	—
	ψ_2	−10.42	0.211	0.130	—	—
	ψ_2^*	3.97	—	—	0.269	0.390
	ψ_1	−9.61	—	—	0.231	0.186
3a	ψ_2^*	2.53	0.208	0.421	—	—
	ψ_2	−11.65	0.267	0.152	—	—
	ψ_1^*	2.27	—	—	0.108	0.193
	ψ_1	−11.24	—	—	0.231	0.186

has been attributed³⁶ to the increased polarisability of the allene system under the influence of substituents, which confirms the transfer of electron density from the allene system to the phosphorus-containing fragment. The dipole moments of PA with identical structure of the allene skeleton increase in the following sequence: esters < acid dichlorides < dimethylphosphine oxides. The dipole moments of allenes mono- and di-substituted at the C(3) atom are somewhat higher.

The molecular electrostatic potential (EP) is used widely to determine the interaction energies in the initial stage of the reaction and the direction of attack on the substrate by charged species.⁶⁰ This quantity is relatively insensitive to the accuracy of the wave functions and the results of calculations by semiempirical methods are comparable to those of *ab initio* calculations.⁶¹

Photoelectron spectroscopy makes it possible to obtain objective information about occupied molecular orbitals.⁶² There are at present no experimental data on this topic. We shall therefore henceforth make use exclusively of the results of quantum-chemical calculations (Table 2).⁴⁹ The first and second unoccupied molecular orbitals of PA are located on one of the double bonds of the allene system. According to *ab initio* calculations in terms of the 4-31 G basis set, the energy of the π_2^* orbital in molecules of the allenes **9** and **10** is lower than that of the π_1^* orbital. The introduction of two Cl atoms into the phosphorus-containing fragment decreases the energies of both lowest unoccupied orbitals in compound **3a**, the influence on the π_2^* orbital being greater. This leads to the inversion of the unoccupied orbitals, but the difference between the energies of the π_1^* and π_2^* orbitals remains small. On the other hand, the population of the $2p\pi$ atomic orbitals of the C(1)=C(2) bond exceeds by a factor of 2 the degree of localisation of the π_2^* orbital of the C(2)=C(3) bond and according to Zverev *et al.*,⁴⁹ this particular orbital actually controls the interaction of the allene **3a** with aryl azides. The AM1 method yields results qualitatively close to the values calculated by the *ab initio* method, although it leads to the inversion of the unoccupied orbitals for the allene **3a**.

According to the calculation in terms of the 4-31 G basis set, the energies of the unoccupied and occupied π and π^* orbitals in the molecules of PA vary in parallel. This made it possible to

Table 4. Chemical shifts (δ) in the ^{13}C NMR spectra of PA and related compounds.

Compound	δ /ppm			Ref.	Compound	δ /ppm			Ref.
	C(1)	C(2)	C(3)			C(1)	C(2)	C(3)	
$\text{H}_2\text{C}(1)=\text{C}(2)=\text{C}(3)\text{Me}_2$	72.1	207.5	93.1	58	$\text{HOPHC}(1)\text{H}=\text{C}(2)=\text{C}(3)\text{H}_2$	92.4	217.5	85.9	58
$\text{Cl}_2\text{PC}(1)\text{H}=\text{C}(2)=\text{C}(3)\text{H}_2$	89.7 (90.0)	212.1 (212.9)	79.3 (80.5)	58 59	$\text{HOPHC}(1)\text{H}=\text{C}(2)=\text{C}(3)\text{Me}_2$	80.8	211.3	99.8	58
$\text{F}_2\text{PC}(1)\text{H}=\text{C}(2)=\text{C}(3)\text{H}_2$	80.9	217.3	78.3	58	$(\text{HO})_2\text{PC}(1)\text{H}=\text{C}(2)\text{H}_2$	129.59	136.67	—	35
$(\text{EtO})_2\text{PC}(1)\text{H}=\text{C}(2)=\text{C}(3)\text{H}_2$	79.8	218.6	75.8	58	$(\text{MeO})_2\text{PC}(1)\text{H}=\text{C}(2)=\text{C}(3)\text{Me}_2$	75.1	209.9	96.0	59
$(\text{EtO})_2\text{P}(\text{Me})-\text{C}(1)=\text{C}(2)=\text{C}(3)\text{H}_2$	88.7	216.0	75.7	58	$(\text{HO})_2\text{PC}(1)\text{H}=\text{C}(2)=\text{C}(3)\text{Me}_2$	80.8	211.3	99.8	59
$(\text{MeO})_2\text{PC}(1)\text{H}=\text{C}(2)=\text{C}(3)\text{H}_2$	77.4	215.5	96.8	58	$(\text{MeO})_2\text{PC}(1)\text{H}=\text{C}(2)=\text{C}(3)(\text{CH}_2)_5$	73.7	205.6	101.2	59
$\text{Cl}_2\text{PC}(1)\text{H}=\text{C}(2)=\text{C}(3)\text{Me}_2$	89.4	209.3	103.8	58	$(\text{MeO})_2\text{P}(\text{Bu}^t)-\text{C}(1)=\text{C}(2)=\text{C}(3)\text{Me}_2$	100.1	206.1	97.1	59
$\text{Me}_2\text{PC}(1)\text{H}=\text{C}(2)=\text{C}(3)\text{Me}_2$	85.4	207.5	96.5	58	$(\text{MeO})_2\text{P}(\text{Bu}^t)-\text{C}(1)=\text{C}(2)=\text{C}(3)\text{HBu}^t$	104.4	205.4	104.4	59

Table 5. The dipole moments (μ) of a series of PA.

Compound	μ /D	Ref.
$\text{H}_2\text{C}=\text{C}=\text{CHP}(\text{OMe})_2$	3.01	37
$\text{H}_2\text{C}=\text{C}=\text{CHP}(\text{OEt})_2$	3.14	36
$\text{H}_2\text{C}=\text{C}=\text{CHPCl}_2$	3.51	37
$\text{H}_2\text{C}=\text{C}=\text{C}(\text{Me})\text{P}(\text{OMe})_2$	3.14	36
$\text{H}_2\text{C}=\text{C}=\text{C}(\text{Me})\text{P}(\text{OEt})_2$	3.07	36
$\text{MeCH}=\text{C}=\text{CHP}(\text{OEt})_2$	3.32	36
$\text{Me}_2\text{C}=\text{C}=\text{CHP}(\text{OMe})_2$	3.46	36
$\text{Me}_2\text{C}=\text{C}=\text{CHP}(\text{OEt})_2$	3.38	36
$\text{Me}_2\text{C}=\text{C}=\text{CHPCl}_2$	4.20	37
$\text{Me}_2\text{C}=\text{C}=\text{CHPMe}_2$	4.70	37
$(\text{CH}_2)_5\text{C}=\text{C}=\text{CHP}(\text{OMe})_2$	3.54	37
$(\text{CH}_2)_5\text{C}=\text{C}=\text{CHP}(\text{OEt})_2$	3.36	37
$(\text{CH}_2)_5\text{C}=\text{C}=\text{CHPCl}_2$	4.59	37

postulate⁴⁹ that, depending on the substituents at the P atom, the above compounds may behave as electron donors or acceptors or can interact *via* a neutral mechanism, as happens for example, in the reaction with aryl azides.¹ The characteristic features of the electronic structure of PA, responsible for their increased reactivity in relation to both nucleophiles and electrophiles, have attracted attention to PA as substrates for the investigation of biphilic reagents.

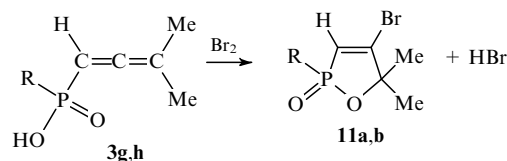
On the basis of the entire set of data examined above, one may postulate that, in contrast to allenes unsubstituted at the C(3) atom, the reactions of 3,3-disubstituted PA with electrophiles occur more readily and, in the case of orbital control,⁶³ selectively with respect to the C(2) = C(3) bond (HOMO). On the other hand, in the case of charge control electrophilic attack should be directed to the C(1) = C(2) bond, where the highest negative charge density is concentrated (Table 2).

Thus, by varying the substituents at the P atom and in the allene system, one may vary the reactivity of both the O atom of the phosphoryl group and of the two double bonds and, if required, one may activate selectively a particular reaction centre.

III. Interaction of phosphorylated allenes with electrophiles

1. Reactions of phosphorylated allenes with the halogens and sulfonyl chloride

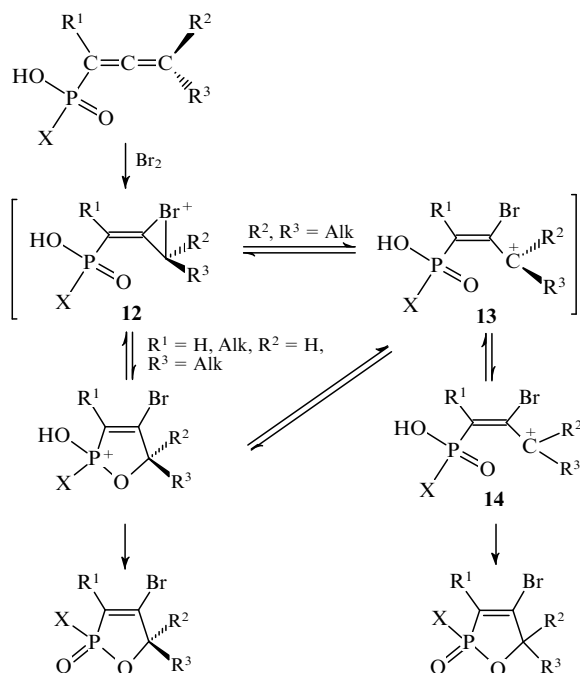
In 1977, Braverman and Reisman⁶⁴ observed that allenylphosphonic and allenylphosphinic acids **3g,h** cyclise on treatment with bromine to 1,2-oxaphosphol-3-enes **11a,b** respectively.



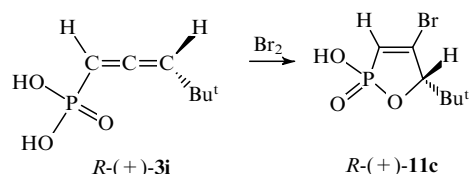
R = Ph (**3g**, **11a**), OH (**3h**, **11b**).

Subsequently it was shown that the bromination of PA monosubstituted at the C(3) atom is also accompanied by a similar cyclisation.⁶⁵

Scheme 1



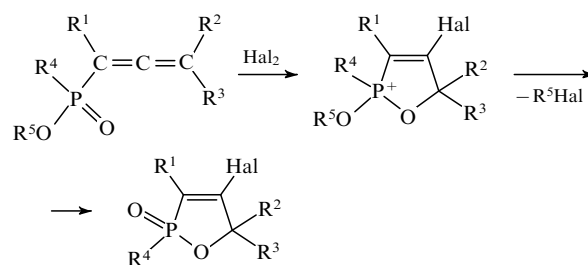
The intermediate formation of the tertiary carbonium ion **14**, in equilibrium with a quasi-phosphonium salt (Scheme 1), the elimination of HBr from which actually leads to the oxaphospholenes **11a,b**, has been postulated.⁶⁴ However, it has been shown⁶⁵ that the bromination of the optically pure acid **3i** takes place with 41% stereoselectivity. This shows that, in the case of allenylphosphonic acids monosubstituted at the C(3) atom, the bromonium ion **12** or the nonplanar secondary carbonium ion **13** is formed as an intermediate rather than the planar carbonium ion **14**. The O atom of the phosphorus-containing group (especially in the case of the *s-cis*-conformation) is capable of trapping the onium ion **12** fairly effectively, which prevents racemisation. The quasi-phosphonium salt formed is unstable and readily eliminates an HBr molecule. It is of interest to note that the bromination of optically active allenecarboxylic acids takes place with approximately the same stereoselectivity,⁶⁶ while in the case of the corresponding allenic alcohols complete racemisation is observed.⁶⁷



The available information about the reactions of free alka-1,2-dienylphosphonic and the corresponding phosphonic acids with the halogens is limited to the two communications mentioned above. The halogenation of esters of these acids has been studied in greater detail.^{64,68–78} For substrates di- and mono-substituted at the C(3) atom, it is also as a rule accompanied by cyclisation (Scheme 2).

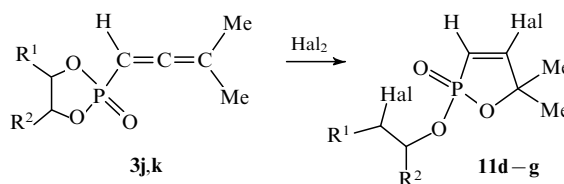
In this case, the reaction also proceeds *via* a stage involving the formation of insufficiently stable quasi-phosphonium salts, which rapidly split off an alkyl halide. The rate of the process depends on the nature of the halogen. On chlorination and bromination, cooling is required (the bromination reaction is weakly exothermic), while on iodination heating is needed. The reactivities of substituted allenylphosphonic esters in relation to interhalogens

Scheme 2



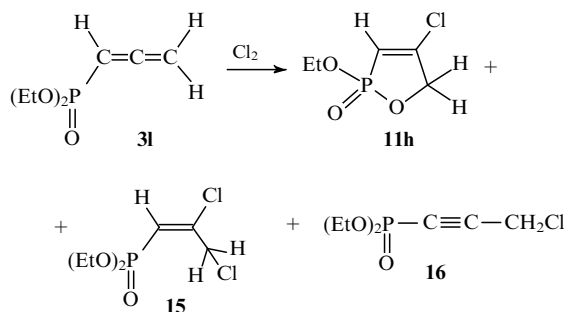
$R^4 = \text{Ph}$, $R^5 = \text{Alk}$; $R^4 = R^5\text{O}$, $R^5 = \text{Alk}$.

have been investigated⁷² and it has been observed that the rate of reaction with ICl is almost twice as high as that with IBr (it is an order of magnitude higher than that for the reaction with I₂).



$R^1 = R^2 = \text{H}$ (**3j**, **11d,f**), Me (**3k**, **11e,g**); $\text{Hal} = \text{Cl}$ (**11d,e**), Br (**11f,g**).

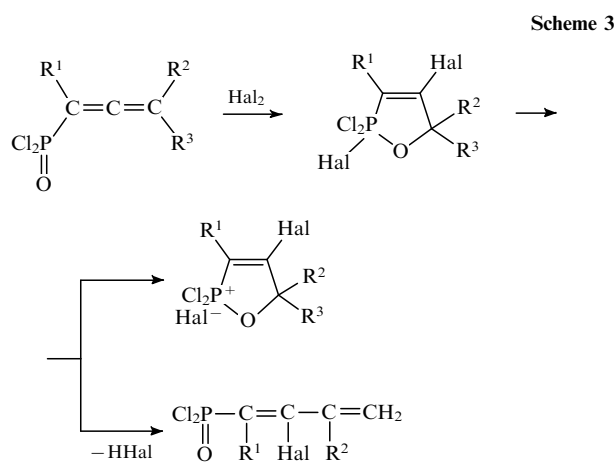
The halogenation of 2-oxo-1,3,2-dioxaphospholanes **3j,k** is accompanied by the opening of the dioxaphospholane ring and the formation of an oxaphospholene ring.⁷⁷ The oxaphospholene **11h** has been detected in a small amount on chlorination of diethyl propadienylphosphonate **3i**, although the main reaction products were found to be the 2,3-adduct **15** and diethyl propynylphosphinate **16**.⁷¹



The different ways in which 3-substituted allenylphosphonic and propadienylphosphonic acids are halogenated shows that the stability of the intermediate type **13** or **14** carbonium ion (see Scheme 1) is one of the decisive factors for the occurrence of cyclisation.

Sulfuryl chloride also reacts with the esters of di- and mono-substituted alka-1,2-dienylphosphonic acids with formation of 4-chloro-1,2-oxaphospholenes,^{79,80} while the reaction with propadienylphosphonic acid esters affords a complex mixture in which adducts formed *via* the C(2)=C(3) bond predominate.⁸⁰

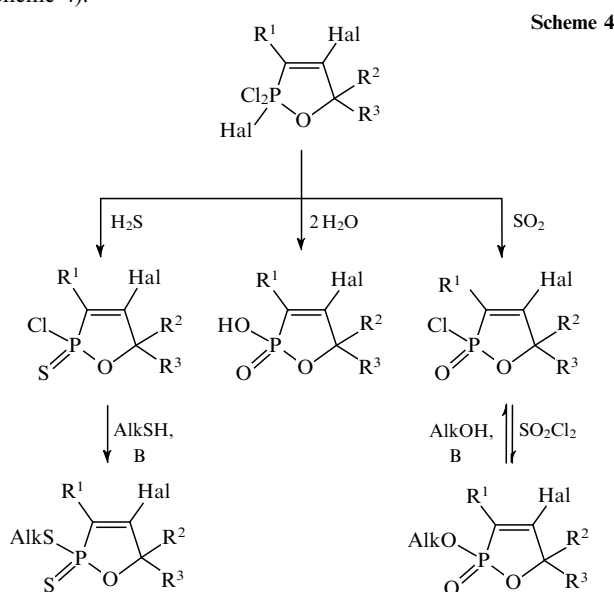
The mode of the halogenation reaction of allenylphosphonic acid dichlorides depends also on the substituents at the C(3) atom of the allene system. In the case of disubstituted allenenes, tetrahalo-1,2-oxaphosphol-3-enes or quasi-phosphonium salts are formed.^{81–90} The tetrahalo-1,2-oxaphosphol-3-enes are stable in nonpolar solvents for several days. After more prolonged storage, they split off the hydrogen halide and are converted into the dichlorides of the corresponding 2-haloalka-1,3-dienylphosphonic acids.^{82,84–91} A proton is split off from the least hydrogenated carbon atom in the substituents R^2 and R^3 (Scheme 3).



$R^1 = \text{H, Alk, Ar; } R^2 = R^3 = \text{Alk; Hal} = \text{Cl, Br.}$

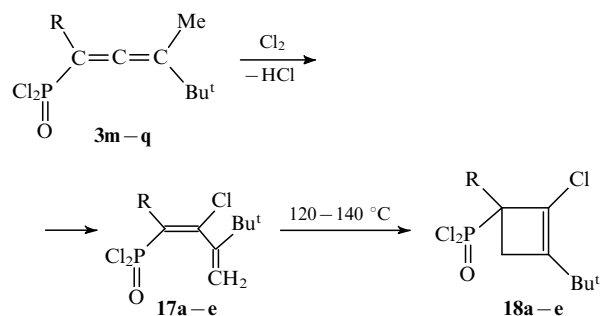
In polar solvents (such as nitromethane, chloroform, *etc.*), the evolution of the hydrogen halide is faster; it is accelerated on heating or removal of the solvent. The process is exothermic, *i.e.* the reaction proceeds in the direction of the thermodynamically more stable product. It is noteworthy that HBr is split off more readily than HCl and in certain cases the intermediate phosphorane cannot be detected. This may be explained by the fact that the bromo-derivatives of pentacoordinate phosphorus have a more polar structure.⁸²

The properties of phosphoranes are characteristic of P^V halides. Thus they readily interact with various nucleophiles (Scheme 4).⁸³



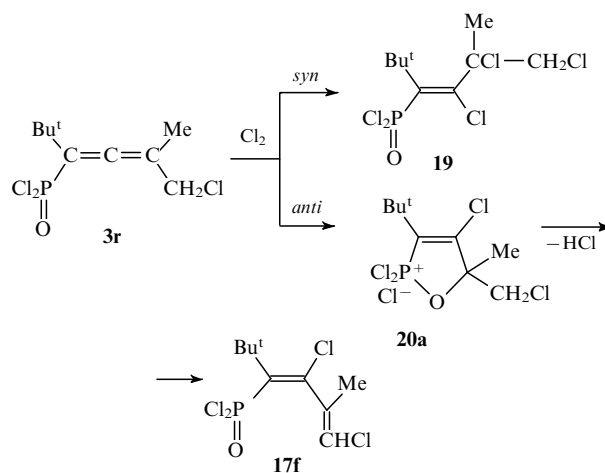
The alka-1,3-dienes formed from phosphoranes have the *s-cis*-configuration of the double bonds. This has been demonstrated by a study of their ^1H NMR spectra with the aid of lanthanide shift reagents⁹¹ and also by studies of the configurations of the products of the reactions of dienes with electrophiles. The halogenation of the alka-1,3-dienylphosphonates obtained by the method described above is accompanied by cyclisation with formation of six-membered heterocycles — derivatives of 5,6-dihydro-2*H*-1,2-oxaphosphorine.^{92,93} The halogenation of alka-1,3-dienylphosphonates synthesised by other methods (having the *s-trans*-conformation) leads not to oxaphosphorines but to the products of the addition of the halogen to the double bond remote from the P atom.⁹⁴ The skewed *s-cis*-conformation of the alka-1,3-diene system may impart also other unusual properties to phos-

phorus-containing alka-1,3-dienes. Thus, when the dichlorides of alka-1,3-dienylphosphonic acids **17a–e**, containing a bulky substituent in the 3-position, are heated, cyclisation takes place readily with formation of the dichlorides of cyclobutenylphosphonic acids **18a–e**.^{95,96}



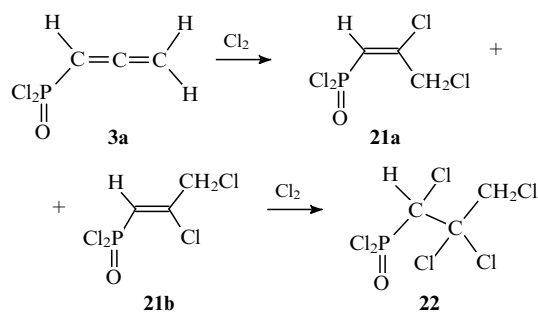
$R = \text{H (3m, 17a, 18a), MeOCH}_2 \text{ (3n, 17b, 18b), ClCH}_2 \text{ (3o, 17c, 18c), Ph (3p, 17d, 18d), } p\text{-MeC}_6\text{H}_4 \text{ (3q, 17e, 18e).}$

The presence of a bulky group in the α -position relative to the P atom promotes an unusual mode of chlorination of the dichloride of 1-*tert*-butyl-4-chloro-3-methylbuta-1,2-dienylphosphonic acid **3r**: the adduct **19**, obtained by addition to the 2,3-double bond, is formed in 42% yield.^{89,90}

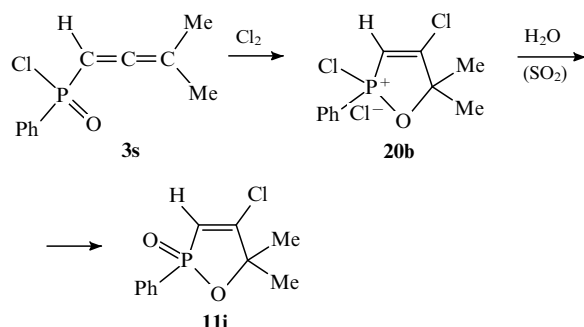


Evidently the presence of this compound can be accounted for by the *syn*-attack by the electrophile relative to the phosphorus atom — a process which is unfavourable in the majority of cases, but in this substrate is caused by the presence of the *tert*-butyl group. In addition, the phosphonium salt **20a** is formed in 39% yield. It is sufficiently stable to be isolated in a pure form. The salt structure of compound **20a** has been confirmed by the chemical shift of the phosphorus signal in the ^{31}P NMR spectrum: $\delta = +93$ ppm.

The *syn*-attack by the electrophile takes place to a slight extent also on halogenation of the dichloride of propadienylphosphonic acid **3a**. It is noteworthy that the cyclisation is not observed also in the case of *anti*-attack relative to the phosphorus atom: this confirms yet again the decisive influence of the alkyl substituents at the C(3) atom on the direction of the process. The halogenation of the allene **3a** takes place only when the temperature is raised to 60–65 °C. One mole of Cl_2 adds to the double bond remote from the phosphorus atom with the predominant formation of a mixture of the dichlorides of 2,3-dichloro-1-(*E*)-propenylphosphonic acid **21a** and the corresponding *Z*-isomer **21b** (with the ratio 40:41 = 5:1). By carrying out the reaction at the same temperature for 8 h, it was possible to obtain the exhaustive chlorination product **22** in 72% yield.⁷¹

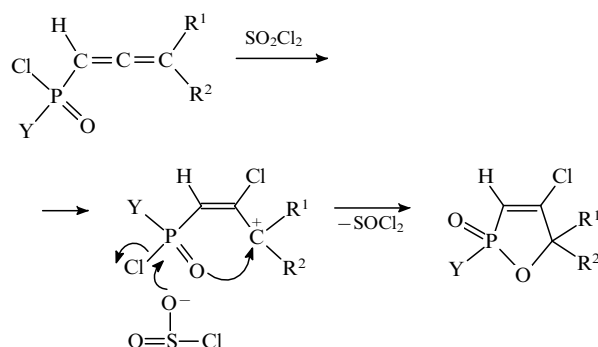


The chlorination of the chloride of 3-methylbuta-1,2-dienyl(phenyl)phosphinic acid **3s** leads to the formation of the phosphonium salt **20b**, which is converted into the oxaphospholene **11i** on interaction with moist air or SO₂. The same chain of reactions occurs on treatment with sulfuryl chloride.⁹⁷



The use of sulfuryl chloride makes it possible to obtain derivatives of 1,2-oxaphosphol-3-ene from the dichlorides of alka-1,2-dienylphosphonic acids not only disubstituted but also monosubstituted at the C(3) atom.⁷⁹ The absence of alka-1,3-dienes of type **17a–e** in these reactions may be caused either by the rapid conversion of the intermediate phosphorane into an oxaphospholene with a tetracoordinate phosphorus atom as a result of the interaction with the SO₂ present in the mixture⁷⁹ or by the fact that the above phosphoranes are not formed at all as intermediates in the given instance. It has been suggested² that the reaction proceeds *via* a stage involving the formation of a carbonium ion with synchronous nucleophilic attack of the O atom of the phosphoryl group on the C(3) atom and of one of the O atoms of the sulfo-group on the P atom. This results in the elimination of the chloride ion and cyclisation (Scheme 5).

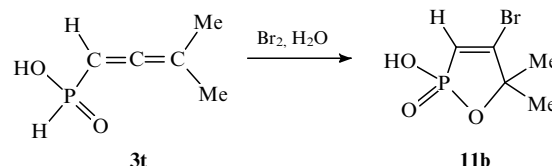
Scheme 5



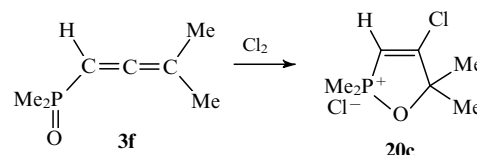
Y = Cl, Ph; R¹ = R² = Alk;
R¹ = H, R² = Alk.

The attack by Cl[−] on the S atom leads to the elimination of thionyl chloride. The chloride of unsubstituted allenylphosphonic acid **3a** reacts with SO₂Cl₂ to form a complex mixture of adducts resulting from addition to the double bonds (as in chlorination by Cl₂).^{71, 79}

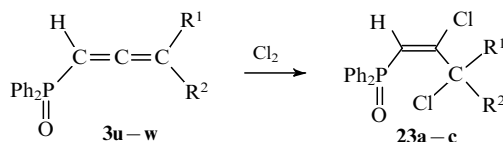
The modes of the reactions of PA with halogenating agents may depend not only on the substituents at the allene system but also on the nature of the groups at the P atom. Thus, in the interaction of 3-methylbuta-1,2-dienylphosphonous acid **3t** with bromine water, the cyclisation is accompanied by the oxidation of the P–H bond.⁹⁸



The halogenation of the esters of alka-1,2-dienyl(phenyl)phosphinic acid disubstituted at the C(3) atom leads to 1,2-oxaphospholenes.⁶⁴ In the reactions of allenylphosphine oxides with the halogens, cyclisation proceeds with formation of stable phosphonium salts, since in this case the stabilisation of the intermediate by the elimination of an alkyl halide is impossible. For example, the product of the reaction of the phosphine oxide **3f** with chlorine in CCl₄ is the cyclic phosphonium salt **20c**.⁹⁷



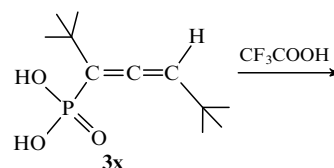
On the other hand, the diphenylphosphine oxides **3u–w** afford under the same conditions the products **23a–c**, which are 2,3-adducts. The observed differences may be explained by the fact that aromatic substituents, conjugated with the oxygen atom of the O=P group, reduce its nucleophilicity. However, according to Angelov *et al.*,⁹⁷ it is more likely that the bulky phenyl groups exert a steric influence on the geometry of the transition state, retarding cyclisation and promoting the addition reaction.

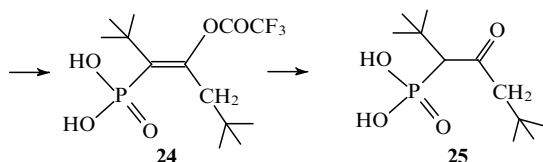


R¹ = R² = H (**3u**, **23a**), Me (**3v**, **23b**); R¹ = H, R² = Me (**3w**, **23c**).

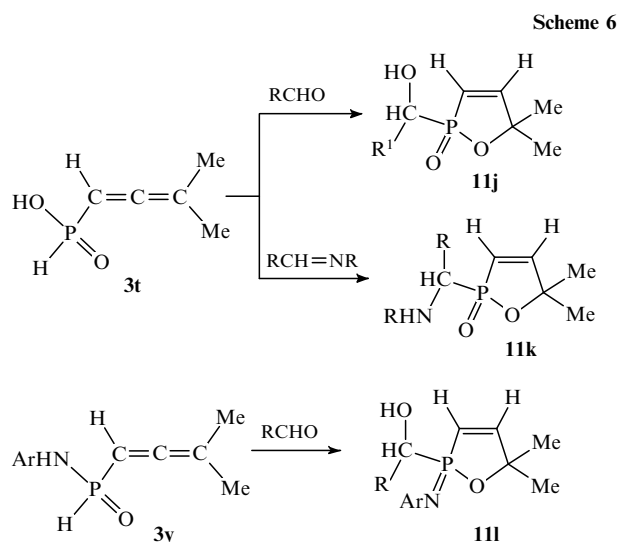
2. Reactions of phosphorylated allenes with proton-donating electrophiles

The study of the reactions of alka-1,2-dienylphosphonic acids with Lewis acids^{99, 100} showed that only the acids disubstituted at the C(3) atom undergo protophilic cyclisation. Propadienylphosphonic acid affords exclusively decomposition products. 1,3-Di-(*tert*-butyl)allenylphosphonic acid **3x** does not interact with HClO₄ in tetrahydrofuran (THF) (18 h, 25 °C), with toluene-*p*-sulfonic acid in a CHCl₃–H₂O mixture (54 h, 25 °C),¹⁰¹ and with 2 M HCl in 80% aqueous diglyme,⁹⁹ while the reaction with trifluoroacetic acid leads unexpectedly to the ketone **25** (in 85% yield).¹⁰⁰ This has been explained¹⁰⁰ by electrophilic attack on the terminal C atom of the allene system.

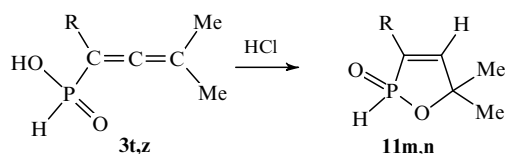




On interaction with carbonyl compounds^{102, 103} and with azomethines,^{103, 104} the acid **3t** cyclises *in situ* with formation of the 1,2-oxaphosphol-3-enes **11j,k** (Scheme 6). The analogous reaction of the corresponding amide **3y** with RCHO leads to the oxaphospholene **11l** containing the O–P=N fragment.¹⁰⁵

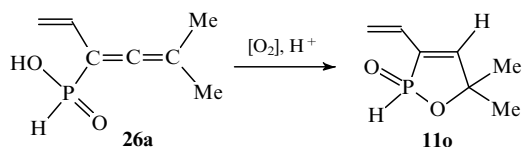


Treatment of 3,3-disubstituted alka-1,2-dienylphosphonic acids **3t,z** with gaseous HCl results in the formation of the oxaphospholenes **11m,n**.¹⁰⁶

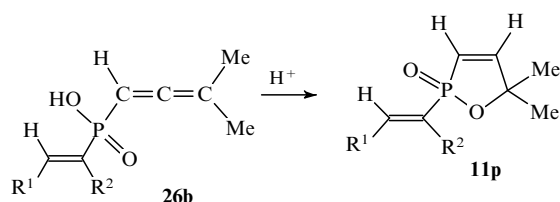


R = H (**3t**, **11m**), Me (**3z**, **11n**).

On treatment with HCl or hypophosphorous acids in the presence of atmospheric oxygen, hexa-1,3,4-trien-3-ylphosphonic acid **26a** cyclises, which is accompanied by the oxidation of the P–H bond.¹⁰⁷



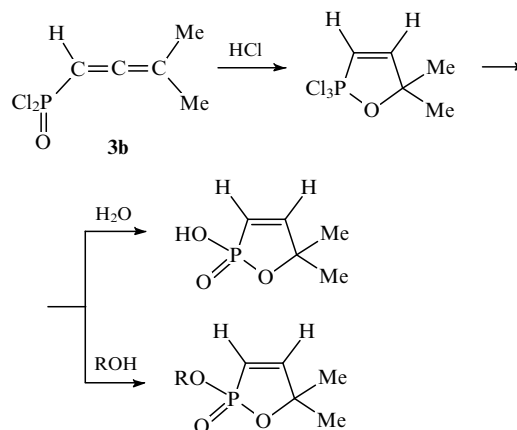
Type **26b** phosphinic acids cyclise to oxaphospholenes above 100 °C in the presence of inorganic acids.¹⁰⁸



R¹ = H, Br; R² = Ph, CH₂Br.

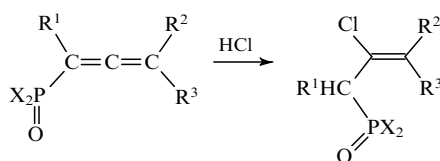
The dichlorides of alka-1,2-dienylphosphonic acids react very slowly with HCl (more slowly than with other electrophiles). After 24 h in inert solvents, the interaction of the chlorides of 3-mono-substituted and 3,3-disubstituted acids with HCl has not been observed.¹⁰⁹ This reaction could be achieved by keeping the mixture in CH₂Cl₂ for 25 days. In the case of the allene **3b**, it proceeds with formation of a cyclic phosphorane,⁹⁹ which, after treatment with water, affords the corresponding acid, while its interaction with alcohols gives rise to esters of this acid (Scheme 7).

Scheme 7



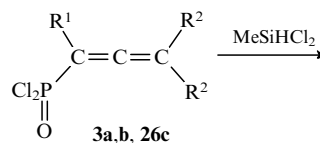
The hydrochlorination of the dichlorides of alka-1,2-dienylphosphonic acids is much faster in the presence of tertiary amines or other aprotic ionising additives, for example, the oxides of tertiary phosphines, hexamethylphosphoramide, *etc.*^{76, 108} However, this reaction proceeds *via* a nucleophilic mechanism and leads to the dichlorides of 2-chloroalk-2-enylphosphonic acids. The corresponding acid difluorides react similarly (Scheme 8).¹⁰⁸ The presence of electron-accepting substituents promotes hydrochlorination. Thus HCl adds to allenes containing the CH₂F group already during their synthesis from acetylenic alcohols and PCl₃ in the presence of pyridine while in the case where the CH₂Cl group is also present the reaction is so fast that the allene itself cannot be isolated.⁷⁶

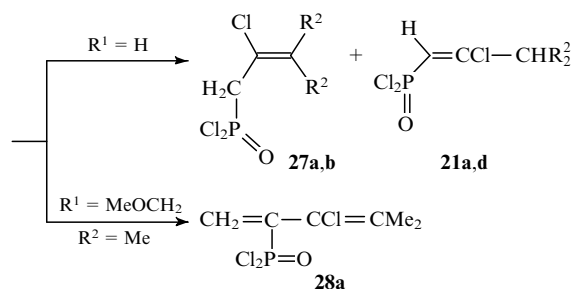
Scheme 8



R¹, R², R³ = Alk, Ar, CH₂Cl, CH₂F; X = Cl, F.

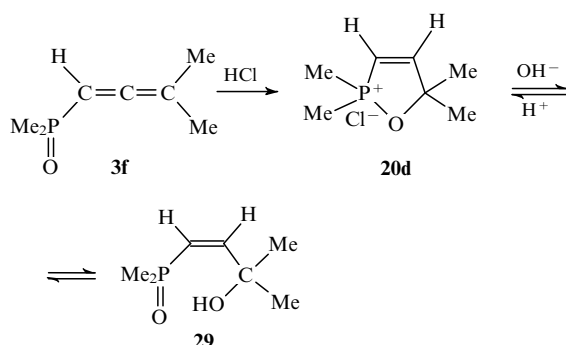
It has proved convenient to employ dichloromethylsilane for the hydrochlorination of the dichlorides of alka-1,2-dienylphosphonic acids **3a,b**. HCl then adds to the α- and β-double bonds.¹¹⁰ The reaction of the dichlorides of 1-methoxyalka-2,3-diene-2-ylphosphonic acids **26c** with dichloromethylsilane leads exclusively to the product **28a** of the allene–1,3-diene isomerisation.⁸⁶





$\text{R}^1 = \text{R}^2 = \text{H}$ (3a, 27a, 21a,b);
 $\text{R}^1 = \text{H}, \text{R}^2 = \text{Me}$ (3b, 27b, 21c,d);
 $\text{R}^1 = \text{MeOCH}_2, \text{R}^2 = \text{Me}$ (26c, 28a).

The hydrochlorination of PA having two or three P–C bonds is accompanied by cyclisation.¹¹¹ In the case of (3-methylbuta-1,2-dienyl)dimethylphosphine oxide **3f**, the quasi-phosphonium salt **20d** is formed. It is relatively stable in inert solvents, but is unstable in water and is in equilibrium with compound **29**. At pH 3, the equilibrium is fully displaced towards the open-chain compound. The ring opening may be regarded as the second stage of the Arbuzov reaction. In the given instance, the above process is reversible and the salt **20d** is reformed on raising the acidity to pH 1.

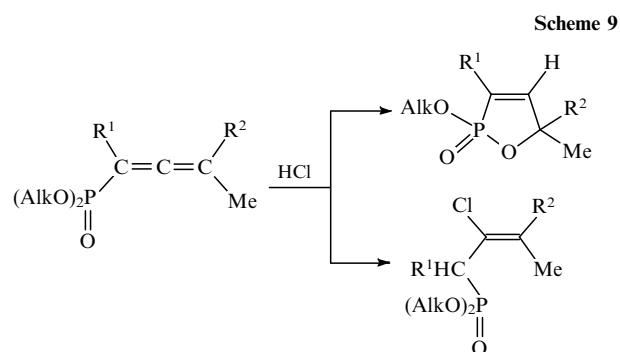


If concentrated H_2SO_4 is used for the cyclisation, it is possible to detect the formation of quasi-phosphonium salts also in the case of the esters of allenylphosphinic and allenylphosphonic acids.^{111,112} On treatment with 40%–70% H_2SO_4 in water or aqueous dioxane, the hydrolysis of the quasi-phosphonium salts is so fast that they cannot be clearly detected. In both cases, the rate-limiting stage is the protonation of the allene to a carbonium ion, after which ring closure takes place with formation of a quasi-phosphonium salt.¹¹¹

The influence of the acidity of the medium, of the isotope effect or the solvent, and of the structure of the phosphorus-containing compound on the rate and direction of the addition reaction has been investigated.¹¹³ The rate constants obtained at different H_2SO_4 concentrations confirm that the reaction is acid-promoted. This is also indicated by the magnitude of the kinetic isotope effect $k_{\text{H}}/k_{\text{D}}$, which is 1.47 for 70% H_2SO_4 and 4.23 for anhydrous trifluoroacetic acid. Thus the cyclisation represents electrophilic addition involving a proton and the substrate in its rate-determining stage. It is noteworthy that the presence of the phosphorus-containing fragment in the substrate is responsible for certain differences from the majority of other reactions involving the conversion of an alkene into a carbonium ion.^{113,114}

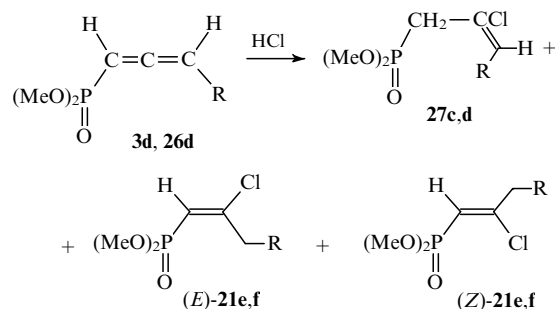
Depending on the nature of the substituent and the solvent polarity, the interaction of esters of 3,3-disubstituted alka-1,2-dienylphosphonic acids with HCl leads to the formation of 1,2-oxaphospholenes or 1,2-adducts (Scheme 9).^{115,116}

In polar solvents, cyclisation takes place exclusively. In non-polar solvents, the reaction proceeds in a more complex manner and 1,2-adducts are obtained together with 1,2-oxaphospholenes. The dimethyl esters of alka-1,2-dienylphosphonic acids, which



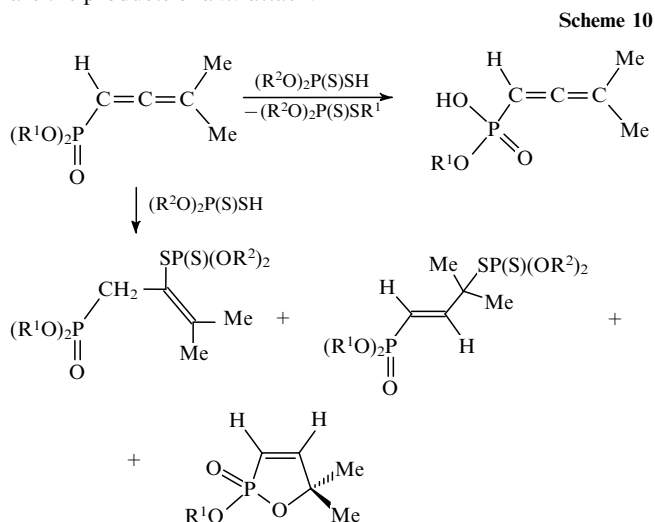
afford only oxaphospholenes regardless of solvent polarity, are an exception. The phenyl substituent in the α -position in the allene system promotes partial hydrolysis of the ester to the corresponding cyclic acid.

Unsubstituted alka-1,2-dienylphosphonates and the derivatives mono-substituted at the C(3) atom (compounds **3d**, **26d**) are not converted into oxaphospholenes even in polar solvents, giving rise to complex mixtures of products in which the adducts **27c,d** predominate.⁶⁵

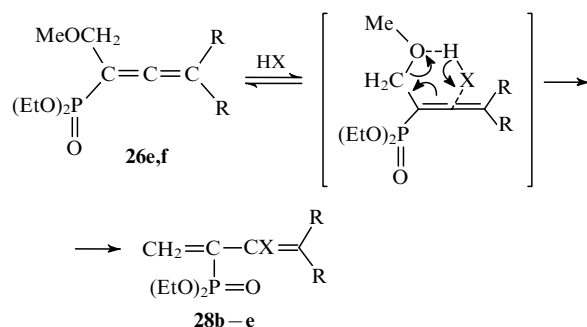


$\text{R} = \text{H}$ [**3d**, **27c**, (**E**)-**21e**, (**Z**)-**21e**], Me [**26d**, **27d**, (**E**)-**21f**, (**Z**)-**21f**].

The interaction of PA with dithio-acids of phosphorus has been investigated.¹¹⁷ Possessing dual reactivity, the acids can add to alkenes *via* both electrophilic and nucleophilic mechanisms. Apart from the products of the addition to the α,β -double bond of the allene (evidently *via* a nucleophilic mechanism) and of the alkylation of the dithio-acid by the alkoxy-group of the initial PA, small amounts of the β,γ -adducts (5%–7%) (Scheme 10) and (or) derivatives of 5,5-dimethyl-1,2-oxaphospholene (5%–6%) have also been detected in the reaction mixture. It is of interest that the 1,2-adducts are formed as a result of *syn*-attack relative to the phosphorus-containing fragment, whereas 1,2-oxaphospholenes are the products of *anti*-attack.

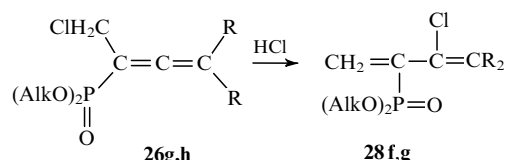


The introduction of functional groups makes it possible to expand still further the range of possible synthetic reactions of PA. The results of the hydrochlorination of 1-methoxybuta-2,3-dien-2-ylphosphonates **26e,f** proved of interest from this point of view.^{118,119} The allene–diene rearrangement, accompanied by the elimination of an alkoxy-group, which results in the formation of 3-halobuta-1,3-dien-2-ylphosphonates **28b–e**, takes place in the course of this reaction. In order to investigate the process mechanism, a study was made of the kinetics of the hydrochlorination of the allenes **26e,f** in various solvents. The activation parameters, the isotope effect, and the influence of the solvent and nucleophilic additives agree with synchronous addition-elimination *via* a cyclic transition state involving the coordination of the acid proton to the ester oxygen and of the halogen to the central carbon atom of the allene system. It was shown that the two alternative mechanisms — the heterolytic mechanism (involving the protonation of the alkoxy-oxygen, the elimination of an alcohol molecule, and the subsequent attack by the nucleophile on the allyl carbonium ion) and the nucleophilic mechanism (*via* the attack of the halide anion on the central C atom of the allene system with subsequent elimination of an alcohol) — are unlikely. Thus the introduction of a new nucleophilic centre — the O atom of the ester group — into the allene promotes a change in the mechanism of the reaction with hydrogen halides.



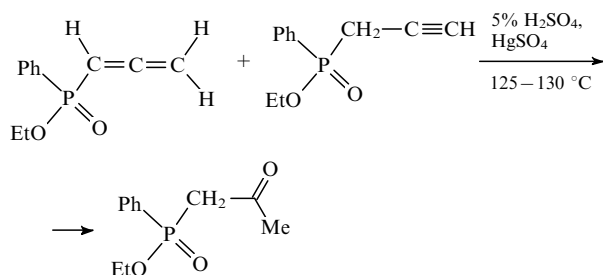
R = H (**26e**, **28b,d**); Me (**26f**, **28c,e**); X = Cl (**28b,c**), Br (**28d,e**).

It has been suggested¹²⁰ that the allene–diene isomerisation of the chloroallenes **26g,h** proceeds similarly.



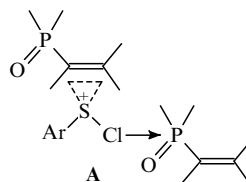
R = H (**26g**, **28f**); Me (**26h**, **28g**).

The hydration of the 1:1 mixture of the ethyl esters of phenylpropa-1,2-dienyl phosphinic and phenylprop-2-ynylphosphinic acids in 5% H₂SO₄ in the presence of catalytic amounts of HgSO₄ afforded ethyl acetonyl(phenyl)phosphinate in 63% yield.¹²¹ In the presence of H₂SO₄ and Hg²⁺ ions, water adds similarly to allenyl(diphenyl)phosphine with formation of β-oxo-phosphine oxide.¹²



3. Reactions of phosphorylated allenes with sulfenyl chlorides

The interaction of sulfenyl chlorides and unsaturated phosphorus-containing compounds proved extremely interesting and made it possible to observe a series of non-trivial effects. For example, the study of the kinetics of this process demonstrated that it proceeds *via* an *Ad_E3* mechanism and that two molecules of the unsaturated phosphorus-containing substrate participate in the formation of the transition state **A** of the rate-limiting stage of the reaction.¹²²

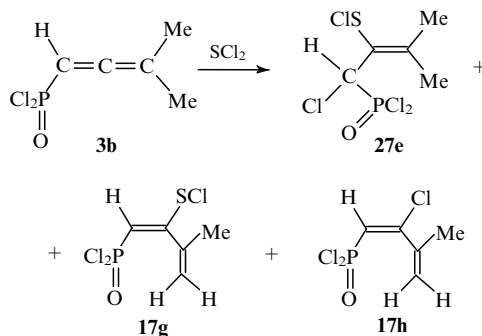


The study of the electrophilic sulfonylation of PA revealed also a series of features not characteristic of reactions of other electrophiles and determined, in the view of the majority of investigators, by the nature of the intermediate species.

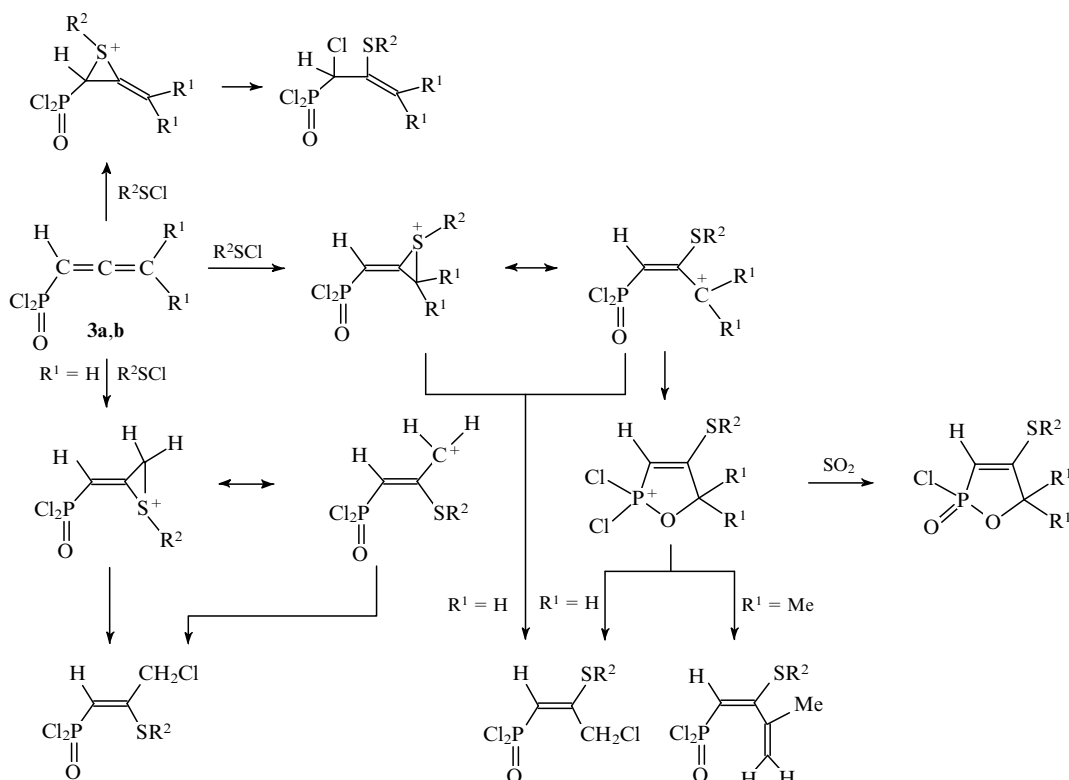
The mode of interaction of sulfenyl chlorides with the dichlorides of alka-1,2-dienylphosphonic acids **3a,b** depends on the presence of substituents at the C(3) atom of the allene system.^{123–128} If the C(3) atom is primary, the reaction leads to 2,3-adducts (with the ratio *E* : *Z* = 85 : 15 in the case of MeSCl or with 100% of the *E*-isomer for PhSCl).¹²⁴ If the C(3) atom is tertiary, then the products are the dichlorides of buta-1,3-dienylphosphonic acids.

The reaction apparently proceeds *via* the formation of an episulfonium ion with its subsequent conversion into a tertiary carbonium ion (Scheme 11). According to a number of investigators,^{1, 124, 125} the reaction proceeds as a rule *via* a cyclic phosphorane intermediate and the formation of different products is determined by the different directions of attack by the chloride ion. The yields of the products of these reactions (57%–63%) are lower compared with the halogenation reaction (85%–95%),^{82–84} which suggests the occurrence of side reactions. Thus it has been shown¹²⁹ that the interaction of the dichlorides of 3,3-disubstituted allenylphosphonic acids **3a,b** and alkanesulfonyl chlorides affords the products of addition to the C(1) = C(2) bond apart from the 1,2-oxaphospholenes. The reaction is carried out in the presence of SO₂ as the fixator of the cyclic intermediate. The ratio of the 1,2-oxaphospholenes and the 1,2-adducts depends on the nature of the substituent at the S atom and on the reaction temperature. The change from R¹ = Me to R¹ = Buⁿ and the lowering of temperature promote an increase in the yield of the 1,2-adducts.

The reaction of SCl₂ with the allene **3b** at room temperature leads to the formation of the adducts **27e** involving the C(1) = C(2) bond and the product **17g** resulting from the elimination HCl in proportions of ~5:3.^{130,131} It is of interest to note that compound **17g** is the first representative of the previously unknown alkadienesulrenyl chlorides. Furthermore, the reaction mixture contains ~5% of the dichloride of 2-chloro-3-methylbuta-1,3-dienylphosphonic acid **17h**.



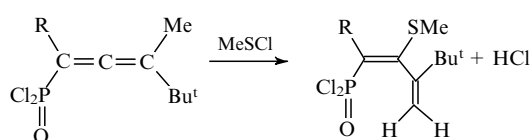
Scheme 11



It is believed¹²⁹ that the ratio of the 1,2-adduct and the cyclisation product reflect the stability of the episulfonium ions relative to carbonium ions. Effective cyclisation requires the formation of a free carbonium ion. In the episulfonium ion, the effective charge on the C(3) atom is reduced, which lowers the rate of cyclisation. Since the electronegative phosphoryl substituent destabilises the episulfonium ion to a lesser extent compared with the 'open-chain' α -carbonium ion, addition to the double bond adjoining the P atom also becomes possible.

In our view, the use in this instance of the concept of the 'episulfonium ion' is not altogether correct, because, firstly, episulfonium ions are fairly polar and sensitive to electronic factors¹³² and, secondly, it had been shown earlier^{132–134} that episulfonium ions are not in reality intermediates in Ad_E reactions of sulfenyl chlorides and the process proceeds *via* the formation of covalent sulfuranes or tight or solvent-separated ion pairs. It is logical to postulate that the intermediates in Ad_E reactions of sulfenyl chlorides with PA should be not sulfonium ions but much less polar structures. It is possible to account in this way for the formation of adducts involving the C(1)=C(2) bond in reactions with PA (although it is not clear why this process becomes dominant in certain cases).

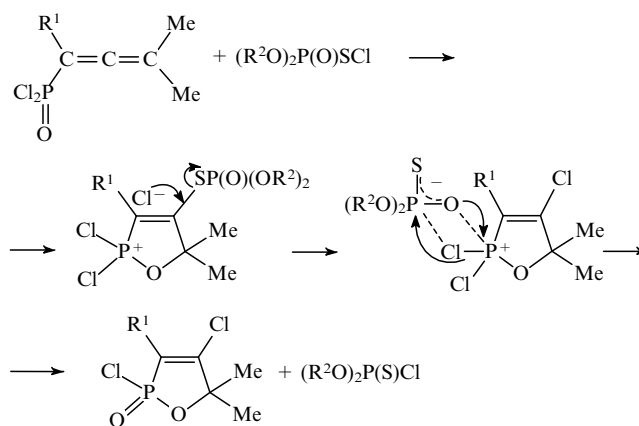
The reactions of the dichlorides of 1-substituted 3-(*tert*-butyl)alka-1,2-dienylphosphonic acid with MeSCl lead exclusively to 1,3-dienes.⁷⁵



R = Ph, MeOCH₂.

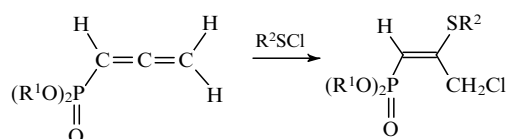
Dialkylphosphorylsulfenyl chlorides react with the dichlorides of alka-1,2-dienylphosphonic acids to form derivatives of 2,4-dichloro-2-oxo-1,2-oxaphospholene (Scheme 12).^{124,125} The interaction of alka-1,2-dienylphosphonic acid esters with sulfenyl chlorides is also determined by the structures of both the allene and the electrophile.

Scheme 12



The data on the reactions of propadienylphosphonic acid esters and R²SCl (R² = Ph, Alk) are contradictory. The structure of the product of addition to the C(1)=C(2) bond in accordance with the Markovnikov rule was initially ascribed to the adduct.¹³⁵ However, subsequently the same workers^{123–125} established the *E*-configuration of the adduct formed by addition to the C(2)=C(3) bond (Scheme 13). 2,4-Dinitrobenzenesulfenyl chloride does not react with PA.¹²⁷

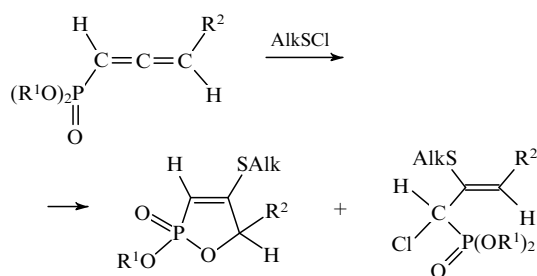
Scheme 13



R¹ = Alk; R² = Alk, Ph.

The interaction of alkanesulfenyl chlorides with propadienylphosphonates monosubstituted at the C(3) atom leads in all cases to a mixture of products of cyclisation and addition to the C(1)=C(2) bond (Scheme 14).¹²⁸

Scheme 14

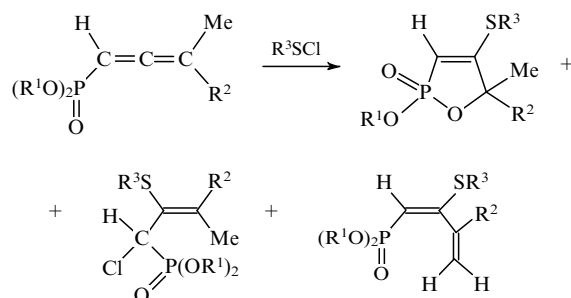


$R^1 = \text{Me, Et, Pr; } R^2 = \text{Me, Pr.}$

However, Khusainova *et al.*¹²⁶ obtained a mixture of the cyclisation products and the 1,2- and 2,3-adducts in proportions of 1 : 1 : 4 as a result of the reaction of buta-1,2-dienylphosphonic acid esters with MeSCl.

Apart from 1,2-oxaphospholenes, the products of the reactions of the dimethyl esters of 3-methylalka-1,2-dienylphosphonic acids with MeSCl are 1,2-adducts (8%–15% for MeSCl) in the form of a mixture of the *E*- and *Z*-isomers in proportions ranging from 1.7 : 1.0 to 5 : 16.¹³⁶ Furthermore, the reaction of dimethyl 3-methylbuta-1,2-dienylphosphonate affords 4%–7% of buta-1,3-dienylphosphonic acid esters (Scheme 15). The isolation of oxaphospholenes alone (63%–82%) had been reported earlier.¹³⁷

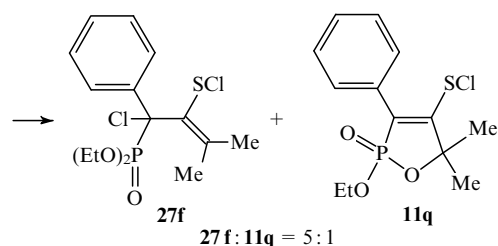
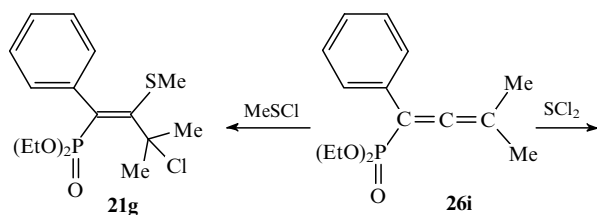
Scheme 15



$R^1, R^2 = \text{Alk; } R^3 = \text{Cl, Me.}$

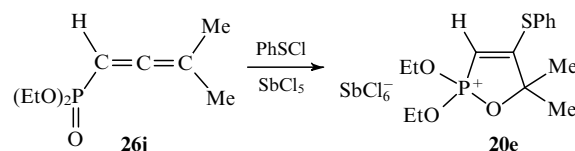
The analogous reaction with SCl_2 proceeds more selectively and leads to 4-chlorothio-1,2-oxaphospholenes in 92%–95% yields.¹³⁸ The latter readily interact with nucleophiles, which makes it possible to introduce the oxaphospholene fragment into a wide range of organic substrates.^{131, 139, 140} The study of the composition of the reaction mixture also made it possible to establish the formation of a 1,2-adduct (1%–2%) and an alkyl-1,3-diene (4%–7%).¹³¹

The principal product of the reaction of 3-methyl-1-phenylbuta-1,2-dienyl phosphonate **26i** with methanesulfonyl chloride is the adduct involving the $\text{C}(2)=\text{C}(3)$ bond.¹²⁸ On the other hand, the interaction of compound **26i** with SCl_2 leads to the formation of predominantly the adduct **27f** involving the $\text{C}(1)=\text{C}(2)$ bond, the structure of which has been confirmed unambiguously by ^{13}C NMR spectroscopic data.¹³¹

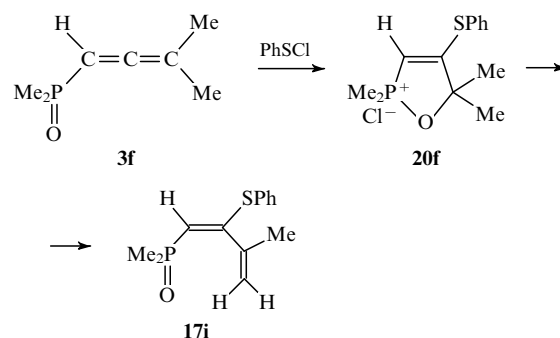


On treatment with alkane(arene)sulfonyl chlorides, allenes containing a bridged substituent in the 3-position afford spiro-linked oxaphospholenes in 71%–90% yield.¹⁴¹ For PA incorporating the 1,3,2-dioxaphospholane ring, the ratio of oxaphospholenes and 1,2-adducts in reactions with alkane-sulfonyl chlorides is 4 : 1, the content of the 1,2-adducts falling to 5% on reducing the temperature from 20 °C to –60 °C.¹⁴²

The stable quasi-phosphonium salt **20e** has been obtained by the interaction of the phosphonate **26j** with benzenesulfonyl chloride in the presence of SbCl_5 .¹⁴³



The reaction of benzenesulfonyl chloride with the PA **3f** leads to the quasi-phosphonium salt **20f** and, when the latter is heated *in vacuo*, HCl is split off and the corresponding 1,3-diene **17i** is formed.¹²⁴

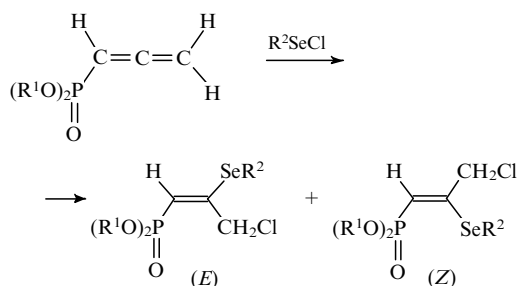


Thus many reactions of PA with sulfonyl chlorides proceed in a manner different from that of the reactions with other electrophiles and a situation which is at first sight paradoxical is observed: the fraction of the adducts involving the $\text{C}(1)=\text{C}(2)$ bond increases with enhancement of the electron-accepting capacity of the substituent at this bond (transition from the dichlorides of allenylphosphonic acids to their esters). It has been postulated hitherto that the main cause of this difference is the possibility of the formation of cyclic intermediates. However, this is insufficient to account for the characteristic features of the reactions described in this section. As an example, we shall consider the interaction of PA and selenenyl chlorides — a class of electrophiles having properties close to those of sulfonyl chlorides, the addition of which to alkenes also proceeds *via* the formation of cyclic intermediates — episelenonium ions.

4. Reactions of phosphorylated allenes with selenenyl chlorides

The mode of the reactions of allenyl phosphonates with selenenyl chlorides also depends both on the structure of the electrophile and on the nature of the substituents at the $\text{C}(3)$ atom of the allene system, but in all cases electrophilic attack is directed exclusively to the $\text{C}(2)=\text{C}(3)$ bond. For example, on treatment with methane-

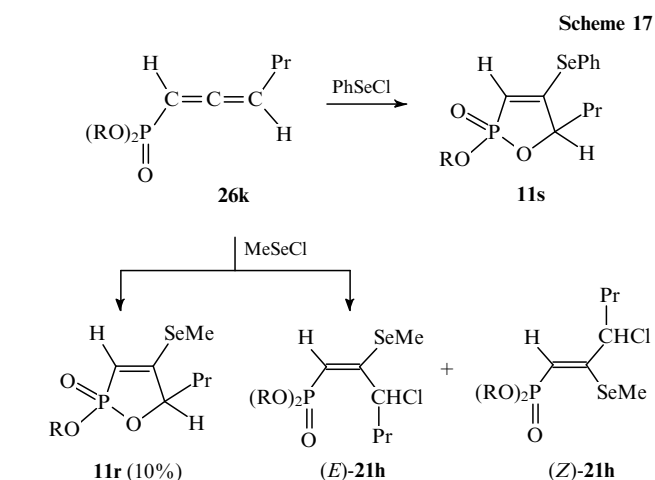
and benzene-selenenyl chlorides, the esters of propadienylphosphonic acid form 2,3-adducts; in the former case, the *E*- and *Z*-isomers are present in comparable amounts, while in the latter the *Z*-isomer predominates.¹⁴⁴ An interesting interpretation of the results of these reactions has been presented by Macomber *et al.*¹²⁷ On the basis of the allyl spin – spin coupling constant (1.5 Hz) and by analogy with the addition of sulfenyl chlorides, the *E*-configuration was attributed to the adduct of dimethyl propadienylphosphonate and benzeneselenenyl chloride (Scheme 16).



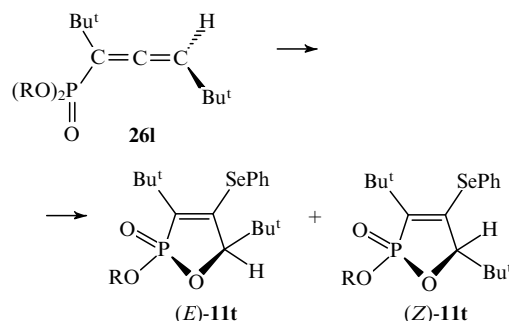
$\text{R}^1 = \text{Alk}; \text{R}^2 = \text{Me, Ph.}$

The interaction of the esters of 3-monosubstituted alkadienylphosphonic acids **26k** with methaneselenenyl chloride also results in the formation mainly of the adducts **21h** involving the $\text{C}(2)=\text{C}(3)$ bond [the *E*- and *Z*-isomers are in proportions of 1 : 3], although the reaction mixture contains also ~10% of the oxaphospholene **11r**.¹⁴⁴ The analogous reaction with benzeneselenenyl chloride led to the isolation of only the oxaphospholene **11s** (Scheme 17).^{127, 144}

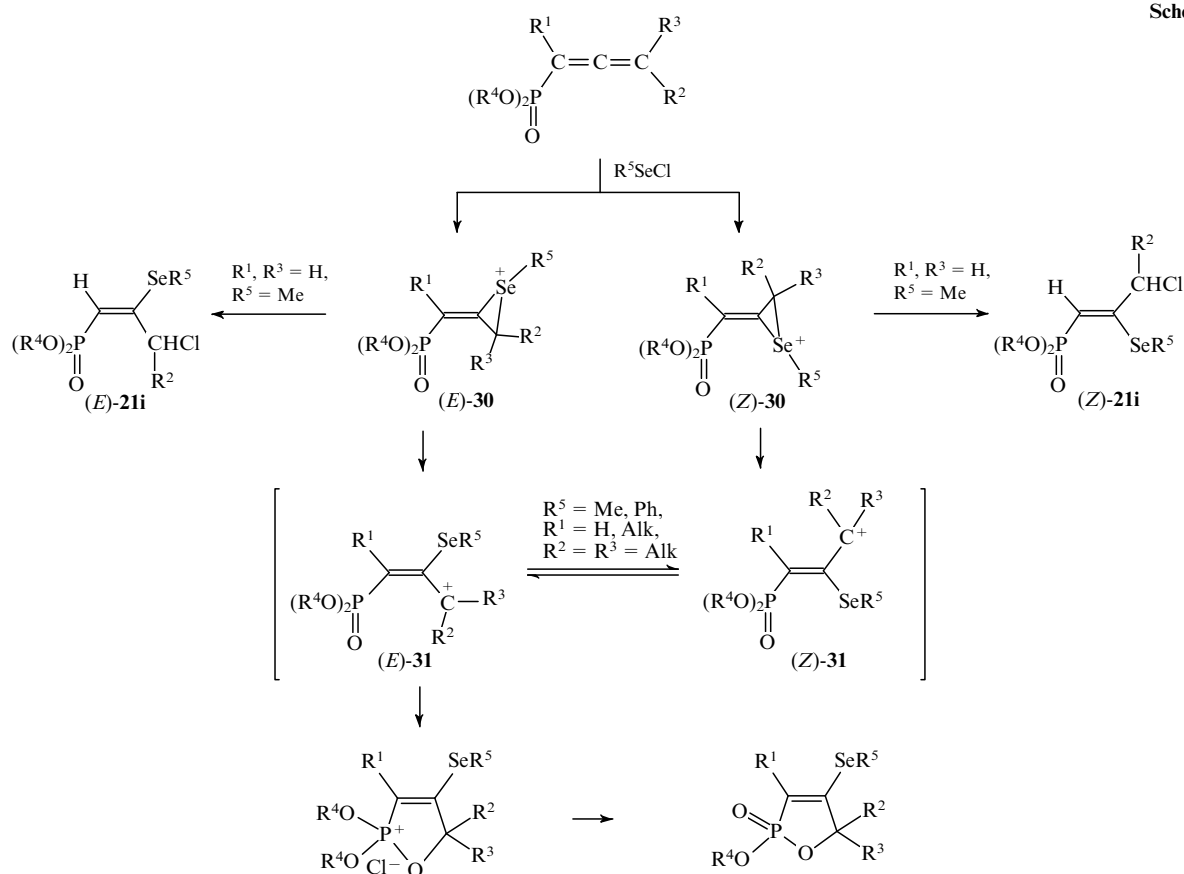
The stereochemistry of the cyclisation of the allenylphosphonate **26l** has been investigated.¹²⁷ The reaction proceeds stereoselectively in acetonitrile [65% of (*E*)-**11t** and 35% of (*Z*)-**11t**], but selectivity is lost on passing to chloroform. This has been



explained¹²⁷ by the different degrees of solvation of the intermediate phosphonium ion.



$\text{R} = \text{Alk.}$



The interaction of esters of alka-1,2-dienylphosphinic and the corresponding phosphonic acids with methane- and benzene-selenenyl chlorides leads exclusively to phospholenes.^{127, 144–146} Thus, in contrast to the reactions of PA with sulfenyl chlorides, in this case the addition to the C(1)=C(2) bond was not observed. The different stereoselectivity of the reactions of selenenyl chlorides has been explained¹⁴⁴ by the influence of the substituents at the Se atom and at the C(3) atom of the allene system on the relative stabilities of the intermediate selenonium and carbenium ions (Scheme 18). According to Angelov and Tancheva,¹⁴⁴ the oxaphospholenes are obtained from the (*E*)-**31** ion, while the 2,3-adducts are derived from the selenonium ions **30**, the preferential formation of the *Z*-isomers¹⁴¹ being associated with the fact that the attack by the chloride ion on the selenonium ion (*Z*)-**30** proceeds more readily, for steric reasons, than the attack on the (*E*)-**30** ion.¹⁴¹

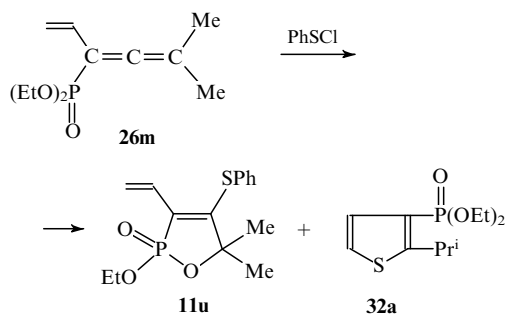
In our view, the mechanism of this reaction is more complex and, as in the case of sulfenyl chlorides, may involve the formation of tight and solvent-separated ion pairs.^{132–134}

5. Reactions of hexa-1,3,4-trienyl and hexa-1,2,4-trienyl-phosphonic acids with sulfenyl and selenenyl chlorides

The introduction into the O=P–C=C=C system of additional nucleophilic centres, which can interact with electrophiles, increases significantly the reactivity of PA. The reactions of vinyl-substituted allenylphosphonates are extremely instructive in this respect.

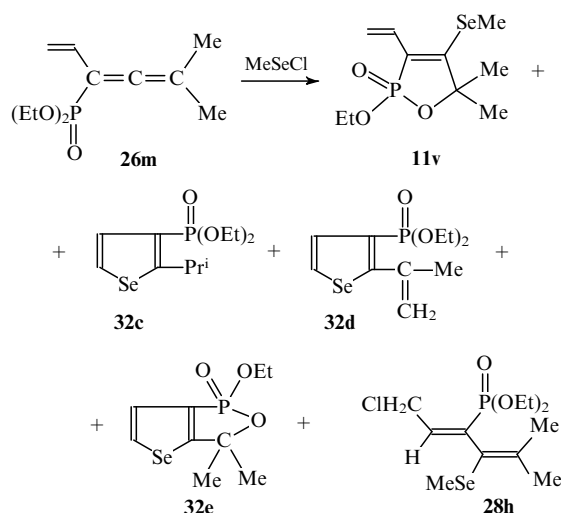
In the interactions with the halogens and sulfur chloride, these compounds exhibit the reactivity typical of allenyl phosphonates, forming derivatives of oxaphosphol-3-enes **11** or alka-1,3-dienylphosphonic acids **17** depending on the substituents at the P atom.^{73, 74, 80, 88}

Diethyl hexa-1,3,4-trien-3-ylphosphonate **26m** reacts similarly with selenenyl chlorides,⁸⁰ but the reaction with sulfenyl chlorides proceeds *via* an unexpected path: together with the 1,2-oxaphospholene **11u**, the thiophene derivative **32a** is formed.¹⁴⁷ The product ratio varies as a function of the reaction temperature: **11u**:**32a** = 1.00:1.33 at 0 °C and 1.25:1.00 at –40 °C.

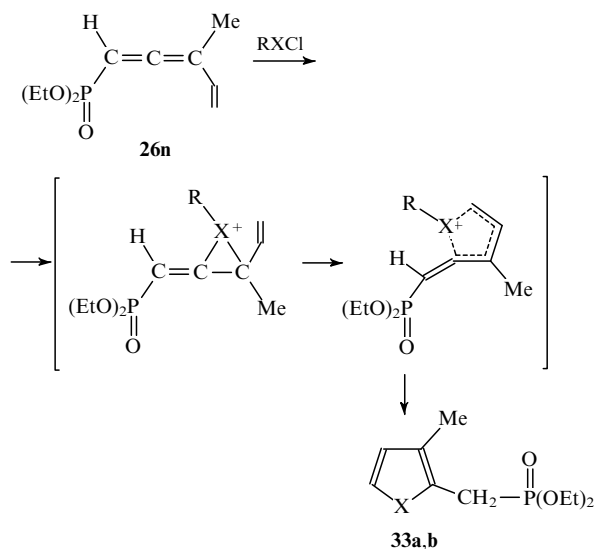


The formation of thiophenes is probably promoted by the same factors as the formation of the 1,2-adducts. This is confirmed, firstly, by the fact that the dichloride of hexa-1,3,4-trien-3-ylphosphonic acid affords exclusively the thiophene derivative **32b** in the analogous reaction¹⁴⁸ and, secondly, by the presence of only traces of similar products in reactions with selenenyl chlorides (see below), for which addition to the C(1)=C(2) bond is uncharacteristic.¹⁴⁴

The interaction of the ester **26m** with selenenyl chlorides¹⁴⁹ leads to the formation of the 1,2-oxaphospholene **11u** as the main product. In addition, the heterocyclic compounds **32c–e** and the 1,4-adduct **28h** were obtained in an overall yield of 5%–12%.

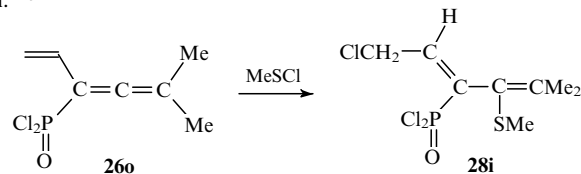


The reactions of diethyl penta-1,2,4-trienylphosphonate **26n** with alkanesulfenyl chlorides open a path to yet another class of substituted thiophenes — 2-thienylmethyl-phosphonic acids **33a**.¹⁵⁰ The interaction of compound **26n** with MeSeCl takes place similarly and leads to 2-selenophenylmethylphosphonic acid ester **33b**.¹⁵¹



X = S (**33a**), Se (**33b**); R = Alk.

The reaction of the dichloride of hexa-1,3,4-trien-3-ylphosphonic acid **26o** with MeSeCl led to the formation of the 1,4-adduct **28i**.¹⁴⁸

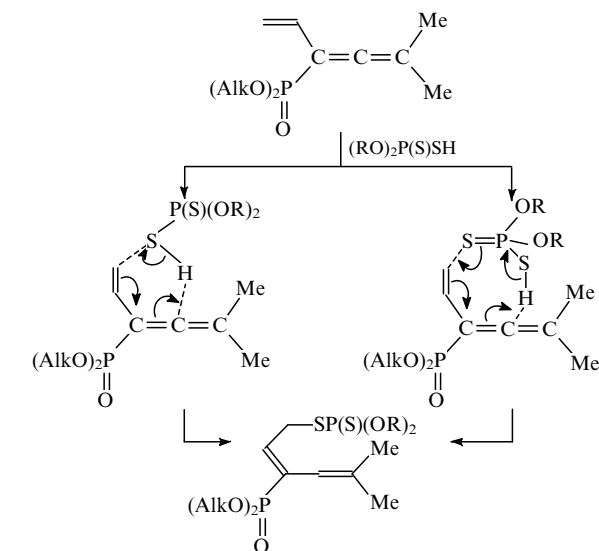


The formation of phosphorylated thiophenes (selenophenes) has been explained^{145, 147–151} by the fact that the intermediate vinylselenonium (episelenonium) ions are capable of expansion to five-membered onium ions. The subsequent isomerisation and

dealkylation afford compounds **32a–c** and **33a,b**. The heterocyclic products **32d,e** are formed similarly.

The interaction of dialkyl hexa-1,3,4-trien-3-ylphosphonates with alkyldithiophosphoric acids has been described (Scheme 19).^{117, 152} The reaction proceeds as addition to the 1,3-diene system. Two alternative mechanisms, involving either a six-centre or eight-centre transition state with participation of the thiol or thione sulfur, are apparently possible.

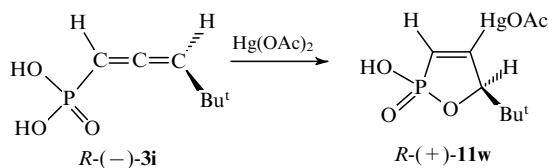
Scheme 19



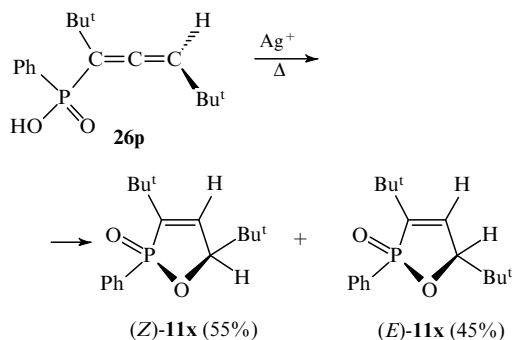
Thus electrophilic attack on the C(1)=C(2) bond is also characteristic of the reactions of the dichlorides of vinyl-substituted PA with sulphenyl chlorides. The presence of functional groups gives rise to the possibility of additional reactions. Yet another direction in which the synthetic possibilities of PA may expand involves the use of new, less traditional electrophiles.

6. Reactions of phosphorylated allenes with other electrophiles

In the course of a study of the cyclisation of the optically active allenylphosphonic acid **3i** under the influence of mercury(II) acetate, it was shown⁶⁵ that it proceeds with 86% stereoselectivity (which is almost twice as high as the selectivity in the bromination reaction).

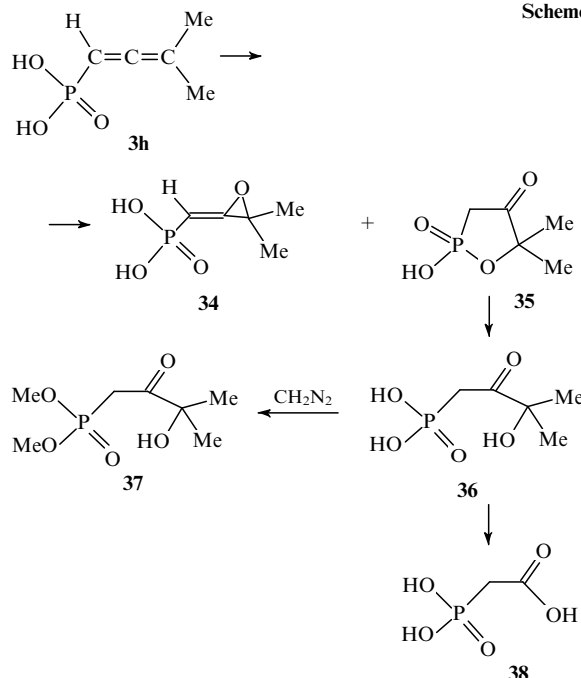


The stereoselectivity of the cyclisation of the allenylphosphonic acid **26p** catalysed by Ag^+ ions has also been studied.¹⁵³

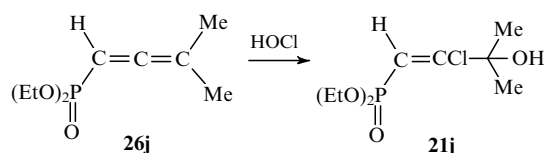


The reaction of the allenylphosphonic acid **3h** with percarboxylic acids has been investigated.¹⁵⁴ Compound **34**, formed initially, isomerises to the oxaphospholane **35**, which hydrolyses with ring opening and is converted into the oxophosphonate **36**. The latter may be converted into the dimethyl ester **37** by treatment with diazomethane or into the acid **38** by treatment with an excess of percarboxylic acid (Scheme 20).

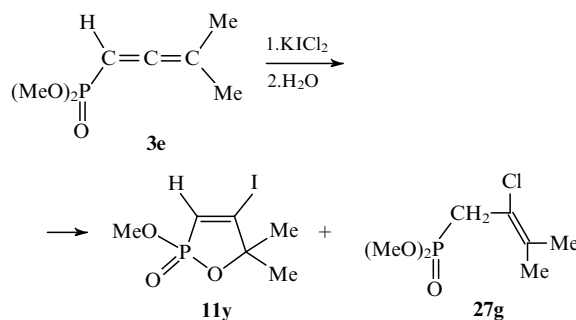
Scheme 20



Hypochlorous acid reacts in an unusual manner with esters of 3,3-disubstituted alka-1,2-dienylphosphonic acids: 2,3-addition with formation of the phosphonate **21j** takes place instead of cyclisation.¹⁵⁵

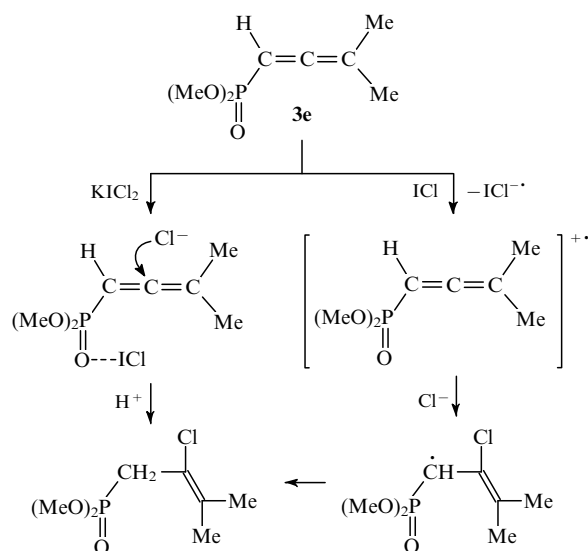


The presence in the molecules of PA of two double bonds with markedly different reactivities, one of which readily interacts with electrophiles whereas the other interacts with nucleophiles, made it possible to observe a new type of reactions of potassium dichloriodate(I).¹⁵⁶ The formation of the main products of the interaction of the PA **3e** with KICl_2 corresponds to the formal addition of iodine chloride *via* the mechanism typical of reactions of electrophiles with the above substrates:



The mechanism of the formation of compound **27g** has not been fully investigated. The regioselectivity of the addition of chlorine indicates that the acyclic phosphonate **27g** is formed as a result of nucleophilic attack by the chloride ion on the α,β -double bond with subsequent protonation of the intermediate. Here it is possible to put forward two versions of the reaction (Scheme 21).

Scheme 21

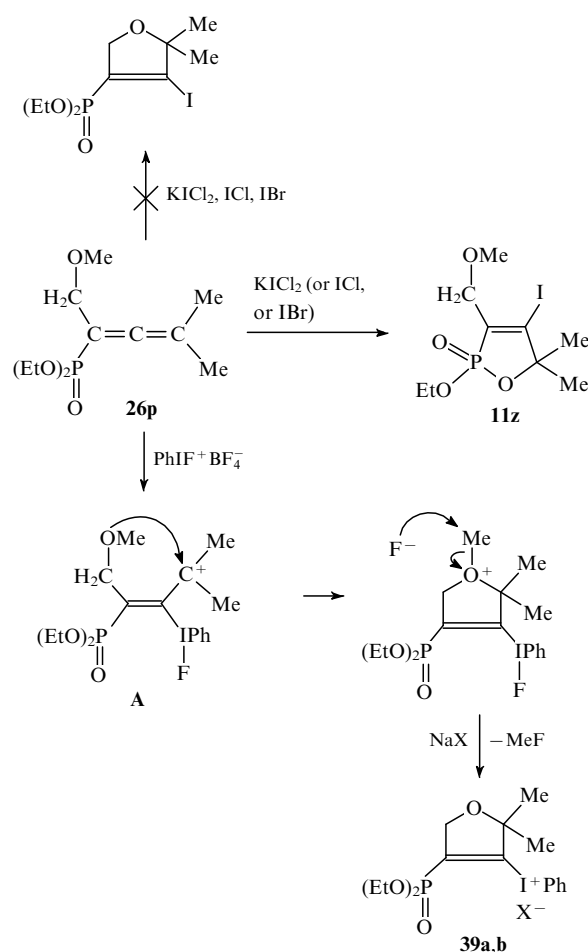


The first involves the nucleophilic addition of the chloride ion, promoted by the coordination of the intermediate iodine chloride, formed from the reagent, to the O atom of the phosphoryl group (ICl is known to exhibit the properties of a Lewis acid¹⁵⁷). The alternative version is the SET mechanism which may occur in reactions of ICl with aromatic substrates.¹⁵⁸

The methoxyallene **26p** reacts with KICl_2 ¹⁵⁶ and interhalogens⁷² with formation of 4-iodo-1,2-oxaphosphol-3-ene **11z**, while its interaction with a more polar iodine-containing reagent (the complex of difluoriodobenzene with BF_3) leads to the dihydrofuran **39a** (yield 63%).¹⁵⁹ The same compound has been obtained by the reaction of the PA **29p** with iodosobenzene in the presence of an excess of BF_3 and subsequent treatment of the reaction mixture with a saturated aqueous solution of NaBF_4 . When a LiClO_4 solution was used, the corresponding perchlorate **39b** was obtained in 48% yield. The addition of the electrophilic iodonium species to the allene **26p** proceeds regioselectively with formation of the stabilised allyl cation **A**. In the concluding stage, the methoxy-group functions as a nucleophile, which is accompanied by the formation of MeF and ring closure to give the furanyliodonium salt **39** (Scheme 22).

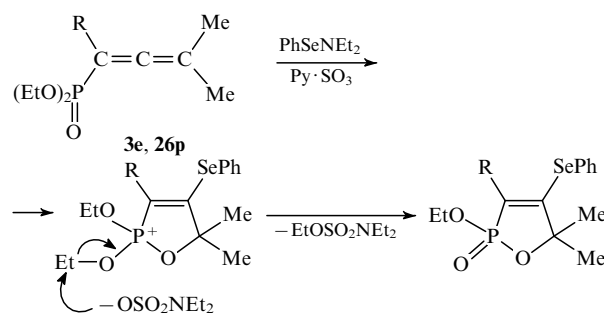
The reaction of *N,N*-diethylbenzeneselenenylamide with the allenylphosphonates **3e** and **26p** in the presence of an activator (a sulfonate), *i.e.* under conditions where weakly polar electrophilic species are generated,^{160,161} proceeds with formation of 1,2-oxaphosphol-3-enes. As in the case of other weakly polar reagents, *anti*-attack by the electrophilic species relative to the phosphoryl residue is observed under these conditions. The subsequent cyclisation evidently takes place *via* the formation of a quasi-phosphonium salt containing the sulfamate ion as the

Scheme 22



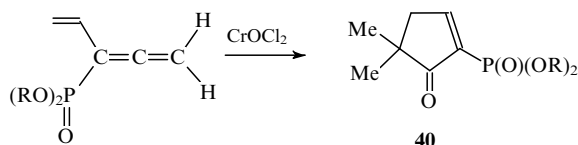
$\text{X} = \text{BF}_4^-$ (**39a**), ClO_4^- (**39b**).

counterion. The nucleophilicity of the latter is sufficiently high for the rapid dealkylation of the quasi-phosphonium salt.



$\text{R} = \text{H}, \text{MeOCH}_2$.

The cyclopentenone derivative **40** can also be synthesised by the interaction of vinyl-substituted PA with chromyl chloride in anhydrous chloroform.¹⁶² As in the reaction with iodonium salts,¹⁵⁹ *syn*-attack by the electrophile relative to the phosphoryl fragment occurs in this case.



R = Alk.

Thus the three examples presented indicate that the stereospecificity of the attack on functionally substituted PA by electrophiles and hence the type of cyclisation are correlated with the polarity of the attacking species. This is probably associated with the fact that more ionic, harder electrophiles are initially coordinated to the O atom of the phosphoryl group. This is indicated by data on the formation of complexes with NiCl_2 ¹⁶³ and also by the results of quantum-chemical calculations (see Section II).

IV. Conclusion

Analysis of the literature data shows that there is a possibility of electrophilic attack on all three reaction centres of the PA depending on the nature of the substituents in the allene system and at the P atom, the polarity of the electrophile, its capacity for preliminary coordination to the internal nucleophilic centres of the PA, and also the stability of the intermediate carbenium, phosphonium, and bridged onium ions. This is promoted by the asymmetry of the allene system, in which the HOMO is localised on the $\text{C}(2)=\text{C}(3)$ bond, although the highest electron density is concentrated on the phosphorus-containing fragment and the $\text{C}(1)=\text{C}(2)$ bond. Whereas positively charged species are coordinated primarily to the oxygen atom of the $\text{O}=\text{P}$ group, uncharged electrophiles may attack either bond of the allene system. With certain exceptions, the electrophilic species then adds to the central carbon atom of the allene system, despite the fact that, according to the results of quantum-chemical calculations^{49, 58} and ^{13}C NMR spectroscopic data,⁵⁹ the electron density on this atom is reduced compared with both terminal carbon atoms. On the other hand, quantum-chemical calculations confirm the presence of a considerable electron density on the $\text{C}(2)$ atom for both the first and second occupied frontier orbitals of the allene [corresponding to a first approximation to the $\text{C}(2)=\text{C}(3)$ and $\text{C}(1)=\text{C}(2)$ bonds].

The molecular orbital perturbation theory may be used to explain and predict the chemoselectivity of the reactions of PA with electrophiles.⁶³ According to this theory, reactions with the early transition state may be controlled either by charge factors or by the interaction of the unoccupied MO of one reactant with the occupied MO of the other. The interaction of the frontier MO is of greatest importance; under these conditions, the greater the difference between the energies of the LUMO of the electrophile and the HOMO of the allene, the more probable is the attack on the $\text{C}(1)=\text{C}(2)$ bond of the PA.

One of the factors influencing significantly the regioselectivity of the attack on the PA by the electrophile is steric hindrance. In the case of the weakest electrophile (the proton), the terminal carbon atom remote from the phosphorus atom is also attacked in reactions with certain monosubstituted PA and PA unsubstituted at the $\text{C}(3)$ atom. The influence of steric factors also on the stereospecificity of the addition when the central atom is attacked is very appreciable. In the addition to the $\text{C}(2)=\text{C}(3)$ bond, the reacting species usually attacks the PA from the side opposite to that of the phosphorus-containing fragment. The introduction of bulky substituents in the 1-position in the allene system increases the amount of the Z-adduct involving the $\text{C}(2)=\text{C}(3)$ bond. Another factor, which probably promotes the *syn*-addition of highly polar electrophiles, is their preliminary coordination to the hard nucleophilic centre comprising the oxygen atom of the $\text{O}=\text{P}$ group. If other nucleophilic centres are present in the PA molecule, there is a possibility of the coordination of the electrophile to

them also, which promotes the operation of additional reaction mechanisms.

Thus, by virtue of the high reactivity and the unusual properties of the system of closely linked unsaturated centres, characteristic of PA, the study of the reactions of these substrates with electrophiles constitutes an extremely interesting and timely problem. The investigation of the reactivities of new electrophiles in relation to PA makes it possible to expand the synthetic possibilities of these processes and to obtain various functionally substituted unsaturated organophosphorus compounds, which are promising from the standpoint of biological activity and their employment in fine organic synthesis. It also aids understanding of the nature of electrophilic processes.

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^b — *Russ. J. Gen. Chem. (Engl. Transl.)*

^c — *Dokl. Chem. (Engl. Transl.)*

^d — *J. Struct. Chem. (Engl. Transl.)*

^e — *Russ. Chem. Bull. (Engl. Transl.)*

Methods of preparation of C-substituted phosphorus ylides and their application in organic synthesis

O I Kolodiazhnyi

Contents

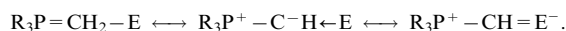
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Abstracts. Methods of preparation of phosphorus ylides substituted at the carbon atom of the P=C group with atoms of various elements and their application in organic synthesis are systematised and generalised. The bibliography includes 508 references.

I. Introduction

During recent years the chemistry of phosphorus ylides substituted at the carbon atom of the P=C group with atoms of various elements has been extensively developed.^{1–14} Owing to these studies, phosphorus ylides containing elements of almost all groups of the Periodic Table have been synthesised, convenient preparative techniques of such ylides have been elaborated, and areas of their practical application in organic synthesis have been discovered. Chemical properties of C-substituted ylides are extremely diverse, which is due to the variety of the properties of the substituent elements and their different effects on the electron density distribution in ylide molecules.

The stability of C-substituted ylides has made them fascinating and convenient objects for theoretical studies, particularly, for the study of the nature of the element–carbocation bond. Depending on the nature of the element, this bond can be covalent or coordinate with various extents of negative charge transfer from the carbanion to the element.



Thus the elements of the higher periods which possess vacant orbitals (silicon, phosphorus, sulfur, arsenic, *etc.*) interact with the ylide carbanion by a $p_\pi-d_\pi$ -mechanism, which results in a decrease in the electron density on the α -carbon atom and partial element–carbon double bonding. On the other hand, the elements with σ -donor properties, *e.g.* mercury, increase the electron density on the ylide carbon, thus increasing further the already high nucleophilicity of ylides. Also certain elements, especially transition metals, can form additional coordinate bonds with the ylide carbon atom. Sometimes, the distribution of the electron density in the ylide molecule is simultaneously affected by two or

even three different factors, their relative contribution depending on the nature of the element and the surrounding ligands.

However, C-substituted phosphorus ylides attract particular interest as reagents for organic synthesis, and thus find increasing application in laboratory practice and industry. For example, C-silicon phosphorus ylides served as the basis for a series of preparative syntheses of medicinals, pheromones, and other types of phosphorus ylides. C-Phosphino phosphorus ylides are important ligands in transition-metal complexes. C-Halogeno phosphorus ylides are of interest for the preparation of halogenoalkenes. C-Nitrogen ylides are of considerable importance, especially in the synthesis of antibiotics. Active catalysts of alkene polymerisation based on C-transition metal-substituted ylides have been proposed. Complexes of phosphorus ylides with gold salts have been recommended for the treatment of certain diseases.

Unfortunately, numerous papers and patents on applications of C-substituted phosphorus ylides in various fields of organic synthesis have not hitherto been generalised. Only some topics concerning the synthesis and chemical properties of C-substituted phosphorus ylides have so far been discussed in monographs^{4, 5, 8, 13} and reviews.^{1–3, 10–12} However, the scope of the topics covered was very narrow, which is due to the specific character of these publications. Also, C-substituted phosphorus ylides are regarded there as a particular case of phosphorus ylides in general. The present review is meant to fill the gap; its aim is to demonstrate the broad synthetic potential of the C-substituted phosphorus ylides and to disclose the effect of the nature of the element at the ylide carbon atom on their reactivity. The present report summarises the data on the application in organic synthesis of phosphorus ylides substituted at the α -carbon atom by atoms of elements of Groups I–VII of the Periodic Table.

II. Phosphorus ylides substituted at the α -carbon atom by atoms of Groups I–IV elements of the Periodic Table

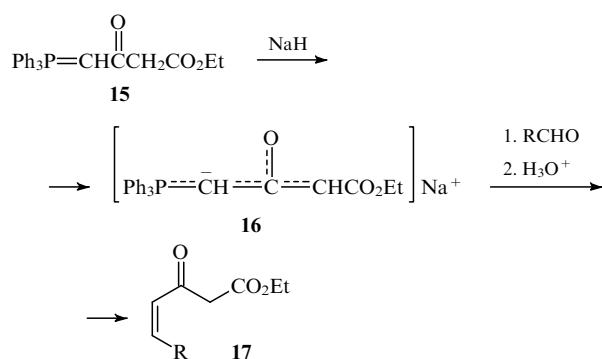
The influence of σ -donor inductive and π -acceptor mesomeric effects of the elements is clearly exemplified by ylides[†] containing metals and metalloids of the main subgroups of Group I–IV of the Periodic Table at the α -carbon atom. The elements with s -donor properties increase the electron density on the ylide carbon atom, thus exchanging the nucleophilicity and reactivity of the ylides, as for instance, in the case of C-lithiated ylides. On the contrary, such elements with as germanium and silicon,

[†] Hereinafter, P-ylides are considered.

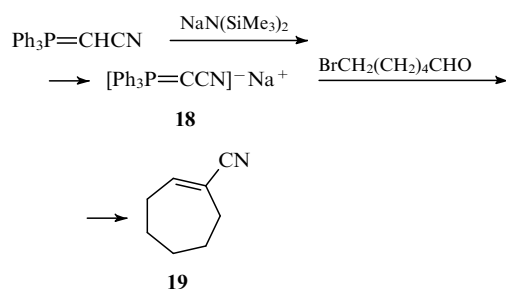
O I Kolodiazhnyi Institute of Bioorganic Chemistry and Petrochemistry, National Academy of Sciences of Ukraine, Murmanskaya ul., 1, 253094 Kiev, Ukraine, Fax (38-044) 543 51 52. Tel. (38-044) 543 52 55. E-mail oik@bpci.kiev.ua

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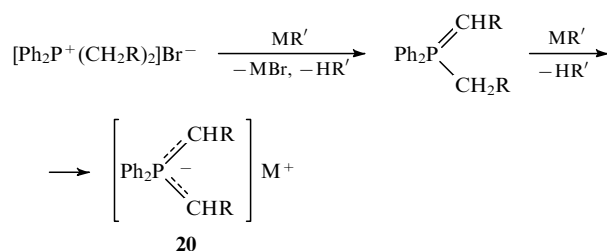
Uspekhi Khimii 66 (3) 246–277 (1997); translated by M I Yanovskaya



The sodium derivatives of triphenylphosphonium cyanomethylide **18** synthesised by Bestmann and Schmidt²⁷ were used for the preparation of cyclic compounds *e.g.*, **19**.

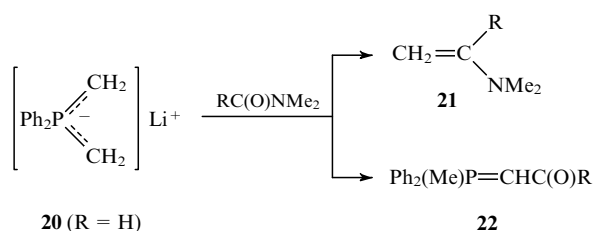


α -Carbon metallated ylide carbanions of the type **20**, which can be obtained by direct addition of 2 equiv. of a base to a phosphonium salt or of 1 equiv. of base to a phosphorus ylide, have recently found an important synthetic application. Some ylide carbanions **20** were isolated in the form of crystalline (colourless or coloured) compounds. Highly reactive tricarbanions were obtained by reaction of trialkylphosphonium ylides with excess of butyllithium.^{14, 21–38} The structures of ylide carbanions **20** were determined by X-ray structural analysis^{39, 40} and NMR spectroscopy.⁴⁰

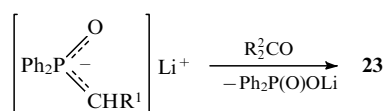
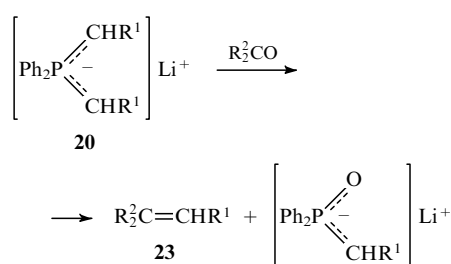


R = H, Ph, CN, CO₂Me;
MR' = KH, NaH, NaNH₂, LiAlk.

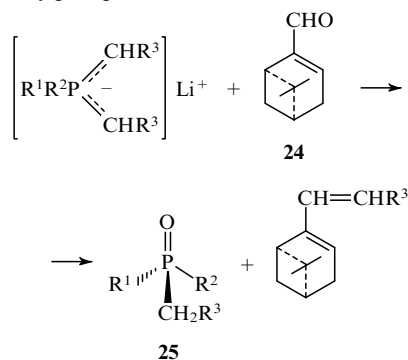
Ylide anions can serve as the initial compounds for the synthesis of other C-substituted phosphorus ylides, because the metal atoms in them are readily substituted for various groups in reactions with electrophiles.⁴¹ Some examples of such syntheses are given in the present review. Ylide anions react even with those electrophiles which do not react, or react with difficulty, with other phosphorus ylides. For instance, they alkenate carboxamides to give enamines **21** or acyl ylides **22** depending on the reaction conditions. Analogously, the reaction of ylide anions **20** with carboxylic esters yields vinylic ethers or acyl ylides.¹⁴



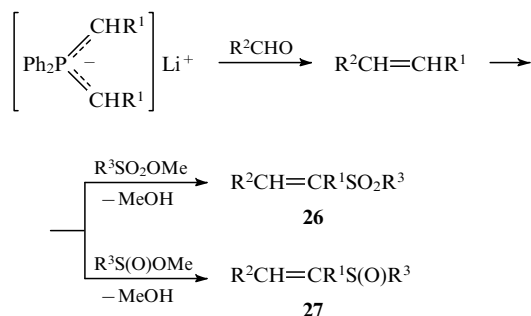
In their reactivity, ylide anions **20** are not inferior in rank to 'hyperactive' C-lithium methylides **2** synthesised by Corey and Schlosser, and they are considerably superior in availability and stability. Thus, ylide anions **20** (R = H)^{42–53} react at room temperature with sterically hindered ketones (di-*tert*-butyl ketone, fenchone), which cannot be alkenated by triphenylphosphonium methylide. The ratio of ylide anion **20** to the carbonyl compound in this reaction is 1 : 2, therefore the yields of alkenes **23** can reach 180%–200% with respect to the phosphorus ylide.⁵⁰



Reaction of ylide anions with chiral aldehydes **24** is accompanied by asymmetric induction, which results in optically active tertiary phosphine oxides **25**.¹⁴



Reactions of ylide anions with aldehydes and carbonates, thiocarbamates, isocyanates, carbodiimides, sulfonates and sulfonates are documented.^{42–53} The two latter reactions give *E*-isomers of the unsaturated sulfones and sulfoxides **26** and **27**.^{50, 52}

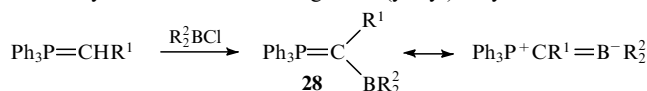


Free ylides containing Group II metals (beryllium, magnesium) at the α -carbon atom have not hitherto been obtained.

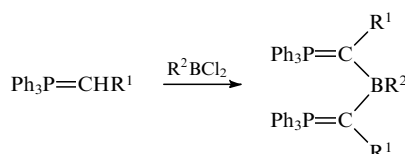
According to the quantum-chemical calculations for the molecule of the simplest ylide $\text{H}_3\text{P}=\text{CHBeH}$, it has planar structure.¹⁶

2. Ylides containing Group IIIA elements

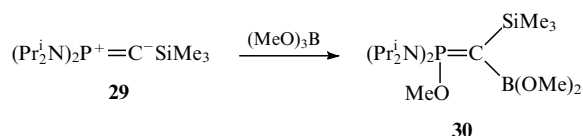
Compounds of elements of Group IIIA of the Periodic Table are strong Lewis acids and readily react with phosphorus ylides.^{54–58} Reactions of triphenylphosphonium alkylides and benzylides with dialkylchloroboranes in benzene are accompanied by transylidation and result in α -dialkylboryl-substituted ylide **28**, which was isolated in the crystalline form. The NMR spectra of the ylide **28** indicate its mesomeric structure.^{58–60} Phosphorus ylides react with alkyl-dichloroboranes to give bis(ylidyl) alkylboranes.



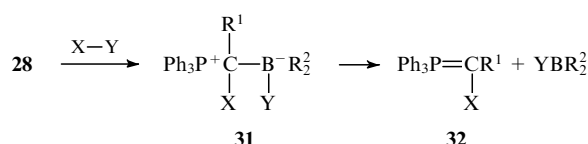
$\text{R}^1 = \text{Alk}, \text{PhCH}_2$.



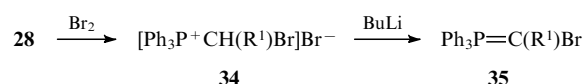
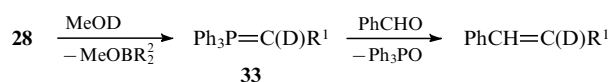
C-Boron substituted ylide **30** was isolated by Bertrand *et al.*⁶¹ by the addition of trimethyl borate to phosphinecarbene **29**:



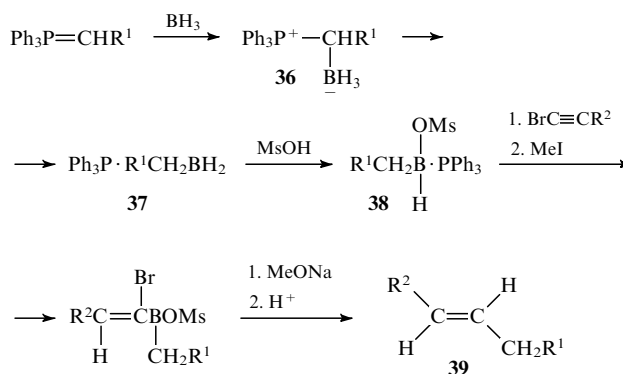
C-Boron substituted ylides **28** are characterised by high reactivity. They readily react with polar compounds $\text{X}-\text{Y}$ to give ylides **32** and boranes *via* the intermediate onium complexes **31**.



Reaction of the ylide **28**, ($\text{R} = \text{Alk}$), with deuteriomethanol gives deuterated ylides **33**, which has been used for the preparation of deuterated olefins. In reaction with bromine, the phosphonium salts **34** were obtained; when treated with butyllithium, they yield C-bromo-substituted phosphorus ylides **35**.⁶⁰



Bestmann and coworkers^{57,62} have elaborated stereoselective methods for the synthesis of *E*-olefins, in particular pheromones, based on products of hydroboration of phosphorus ylides. The key step in the synthesis is the reaction of phosphorus ylide with borane. Betaine **36** thus formed undergoes rearrangement into the adduct of monoalkylborane with triphenylphosphine **37**. The latter is converted to *E*-olefin **39** with 99% stereochemical purity by a series of successive reactions.

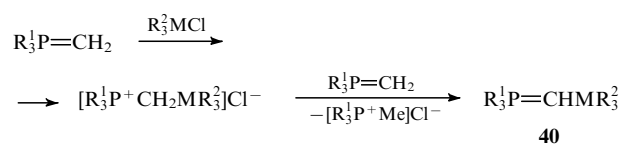


The attempts to synthesise phosphorus ylides with aluminium, gallium, indium, and thallium at the α -carbon atom have failed. The corresponding ylides were unstable and were converted into dimers and oligomers with the structure of metallacycles.^{1,3,63–65}

3. Ylides containing Group IVA elements

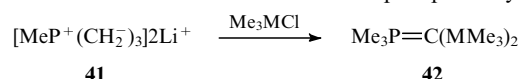
C-Silyl-substituted phosphorus ylides are of considerable preparative importance. The interest in these compounds is due to their availability, stability, and high reactivity. C-Germanium- and C-tin-substituted phosphorus ylides are less studied.

For the synthesis of C-substituted phosphorus ylides **40**, reactions of simple phosphorus ylides containing hydrogen atoms at the α -carbon atom with silicon, germanium, and tin halides (at a 2:1 ratio of the reagents) are most often used.^{66,67} Numerous examples of the synthesis of cyclic and acyclic C-silyl-substituted phosphorus ylides by this method have been reported.^{1,66–73}



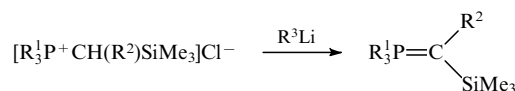
$\text{M} = \text{Si}, \text{Ge}, \text{Sn}$.

Reactions of carbanions **41** with silicon, germanium, tin, and lead halides in a 1:1 ratio lead to the formation of C-mono- or C-dimetal-substituted phosphorus ylides **42** in high yields, which allow a more economical use of the initial phosphorus ylides.^{74–77}

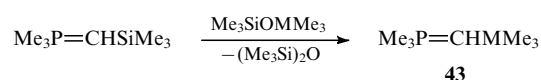


$\text{M} = \text{Ge}, \text{Si}, \text{Sn}, \text{Pb}$.

C-silyl-substituted ylides are often prepared by treating the corresponding phosphonium salts with organolithium compounds.^{66–78}



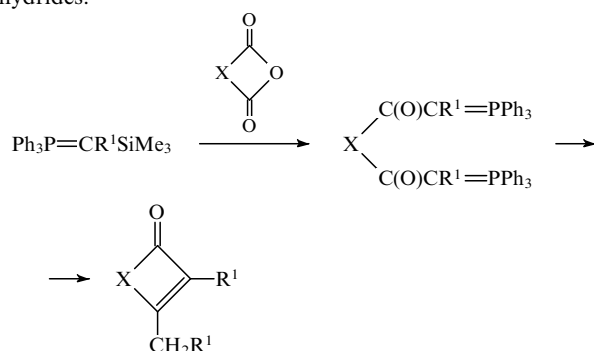
The reaction of trimethylphosphonium trimethylsilylmethylide with heterosiloxanes provides a simple and convenient route to germanium-, tin-, and lead-containing ylides **43**. The driving force of this reaction is the formation of disiloxane.^{74,79}



$\text{M} = \text{Ge}, \text{Sn}, \text{Pb}$.

Silicon-containing phosphorus ylides can be also prepared by the reaction of phosphorus alkylides with silacyclobutane derivatives as a result of the insertion of the ylide carbon atom into the Si–C bond.^{80–82}

The reaction of C-silyl-substituted phosphorus ylides with carboxylic acids proceeds in a similar manner. Cycloalkenones **66** containing 5–8 atoms in the ring were also prepared in high yields by reactions of C-silyl-substituted phosphorus ylides with acid anhydrides.⁷¹



$R^1 = \text{H, Alk; } X = (\text{CH}_2)_n \text{ (} n = 2-5 \text{), CH}_2\text{OCH}_2, \text{CH}_2\text{SCH}_2.$

The reaction of C-silyl-substituted phosphorus ylides with silyl carboxylates has served as the basis for the development of a method of synthesis of ceramide, leucotriene **A₄**^{111–113} and the components of the *Manica ribuda* ant pheromone.¹⁰⁵

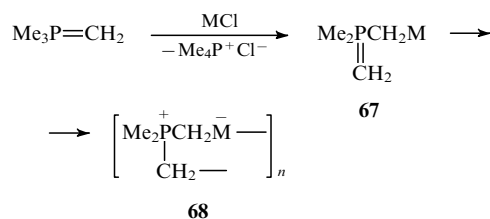
C-Silyl-substituted phosphorus ylides are used as ligands in transition metal complexes. Stable organometallic complexes, with metal–carbon bonds are formed in reactions of C-silyl-substituted phosphorus ylides with halides of copper(I), silver, gold, and their phosphine complexes.^{114–116} Neutral complexes of iron, chromium, molybdenum, and tungsten were also synthesised.^{117–122} Examples of C-silyl-substituted complexes are discussed in the next section and in reviews.^{1–4}

III. Phosphorus ylides substituted at the α -carbon atom by transition metal atoms

Transition metal atoms at the ylide carbon atom substantially affect its negative charge, and consequently, the properties of the ylides. Three main mechanisms describing the interaction of transition metals with the ylide carbanion may be distinguished. Transition metals with s -donor properties, such as mercury, increase the electron density on the ylide carbon atom and enhance the nucleophilicity of the ylides. The electron density on the α -carbon atom decreases if the electron interaction of transition metals with the ylide carbanion, is of d_π – p_π type and the metal–carbon bond acquires partially double character. The relative contribution of these two opposite effects depends on the nature of the metal atom and the surrounding ligands. Finally transition metals can form additional coordinate bonds with the ylide carbon atoms, which may lead to dimerisation or oligomerisation of the organometallic complexes.

1. Ylides containing atoms of Group IB, IIB

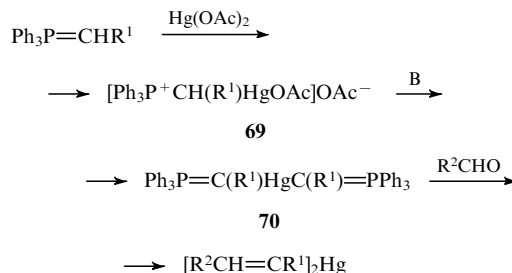
The reactions of phosphorus ylides with copper, gold and silver halides are accompanied by the formation of the ylides **67**, which are easily dimerised into linear and cyclic complexes **68** due to high coordination number of the metal atoms.^{115, 116, 123–125}



$M = \text{Ag, Cu.}$

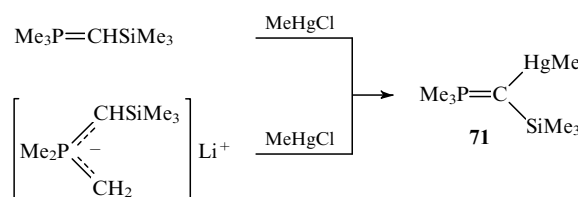
Therefore it was impossible to isolate true ylides of the type **67**. In contrast, C-mercury-substituted phosphorus ylides are mono-

mers. As has been mentioned, mercury atoms increase electron density at the ylide carbon due to their s -donor properties. Therefore, it is necessary that a second substituent at the α -carbon atom should compensate the electron-donating effect of the metal atom in order to stabilize mercurated ylides. Benzoyl, cyano- or methoxycarbonyl groups may serve as such substituents. For instance, phosphorus ylides $\text{Ph}_3\text{P}=\text{CHR}^1$ add mercuric acetate (or chloride) to form compounds **69**; their subsequent reaction with liquid ammonia or sodium methoxide leads to the C-mercurated phosphorus ylides **70**, which enter into the Wittig reaction with aldehydes.^{126, 127}

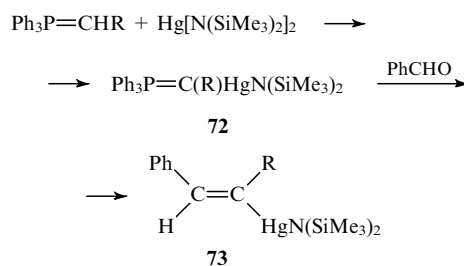


$R^1 = \text{CN, CPh, CO}_2\text{Me; } B = \text{NaOMe/MeOH, NH}_3.$

C-mercurated ylides **71** were obtained by the reaction of methylmercury chloride with an excess of C-silylated phosphorus ylide or its anion. The ylides **71** are stable liquids, which can be distilled *in vacuo*.¹²⁸



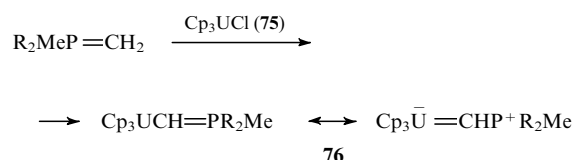
The C-mercury-substituted ylides **72**, which readily enter into the Wittig reaction to form the compounds **73**, were obtained by the reaction of phosphorus ylides $\text{Ph}_3\text{P}=\text{CHR}$ with mercury hexamethyldisilazide in inert solvents.¹²⁹



Other Group IIB metals, zinc and cadmium, give ylide complexes of the type $[\text{Ph}_3\text{PCR}_2\text{MCl}]^+\text{Cl}^-$ ($M = \text{Zn, Cd}$) (**74**). Although the latter cannot be regarded as true ylides, they readily enter into the Wittig reaction and are widely used for the preparation of alkenes,^{130–143} for instance, halogenoalkenes (see Section III.3).^{54, 141–143}

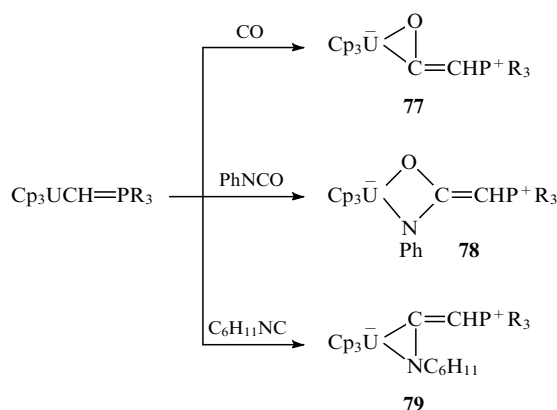
2. Ylides containing atoms of the actinide metals

The uranium complex Cp_3UCl **75** readily undergoes transylidation under the action of phosphorus ylides and their lithium derivatives to form pyrophoric, green crystalline complexes sensitive to moisture and atmospheric oxygen. On the basis of X-ray^{144–146} and electron diffraction¹⁴⁷ data, the metallocene ylide structure **76** was ascribed to these compounds. Shortening of the U–C and C–P bonds indicates the delocalization of the negative charge in the U–C–P fragment.^{145, 147}

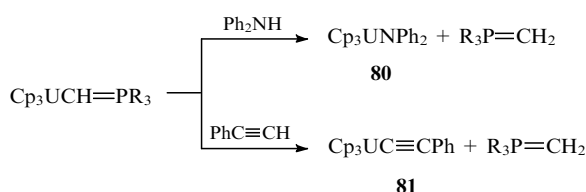


R = Me, Ph.

The metallocene ylides exhibit nucleophilic properties in reactions with polar unsaturated compounds.¹⁴⁶ Insertion reactions into the metal–carbon bond are characteristic of the uranocene ylides.¹⁴⁸

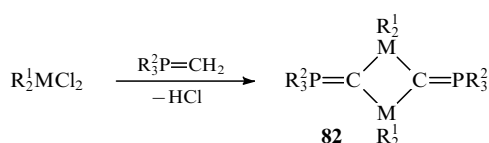


The uranocene ylides enter into metathesis reactions with compounds containing active hydrogen atoms.^{149, 150}



3. Phosphorus ylides containing the Group IVB metal atoms

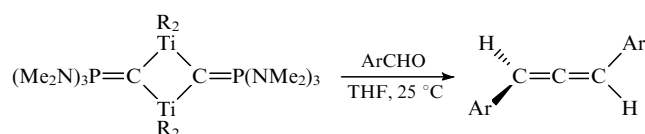
The group IVB transition metals (titanium, zirconium, and hafnium) stabilize the ylide carbanion as do the non-transition elements of this group, silicon and tin. Therefore, the preparation procedures, structures, and properties of phosphorus ylides, which contain metal atoms of Group IVA and IVB at the ylide carbon atoms, are similar. For instance, the four-membered cyclic bis-ylides **82** containing titanium or zirconium atoms at the ylide carbon atoms are obtained in the same way as cyclic silyl-substituted phosphorus ylides. The X-ray structural study of phosphorus ylides **82** has shown that they have a centrosymmetric structure.^{116, 151, 152}



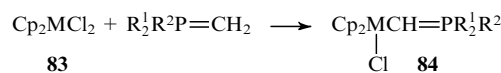
M = Ti, Zr, Hf;

R¹ = Me₂N, Cl, Et; R² = Me, Et₂N, (CH₂)₂PM₂.

The titanium-containing cyclic ylides enter into the Wittig reaction with aromatic aldehydes to form the corresponding 1,3-diaryllallenes which is a promising way for their synthesis.¹⁵³



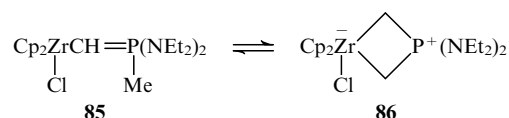
The transylidation reaction of bis(cyclopentadienyl)titanium, -zirconium, and -hafnium dihalides **83** with phosphorus ylides results in C-metallated ylides **84** containing halogen at the metal atom and exhibiting special chemical properties.^{154–160}



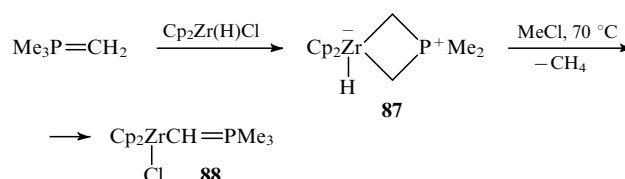
M = Ti, Zr, Hf;

R¹ = R² = Ph, Et₂N; R¹ = Et₂N, R² = Me.

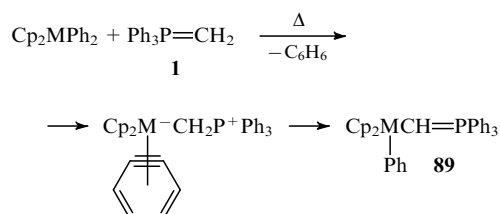
For example, the zirconocene ylide **85** exists in a ring-chain, prototropic tautomeric equilibrium with the chelate complex **86**. The position of the tautomeric equilibrium depends on the nature of the solvent.¹⁵⁶



A zirconium hydride complex reacts with trimethylphosphonium methylide to give a four-membered cyclic ylide complex **87**, which is converted to zirconium ylide **88** on heating with methyl chloride.^{156–158}

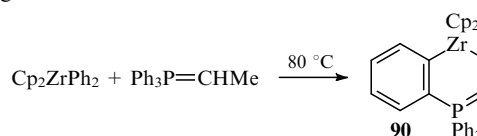


The metallocene ylides of titanium, zirconium and hafnium **89** are formed in the reactions of triphenylphosphonium methylide **1** with the thermally generated (η²-ethene)- and (η²-aryne)metallocenes. These reactions are accompanied by the replacement of the aryne ligand by phosphorus ylide and by a proton shift from the ylide methylene to the aryne ligand.^{159, 160}

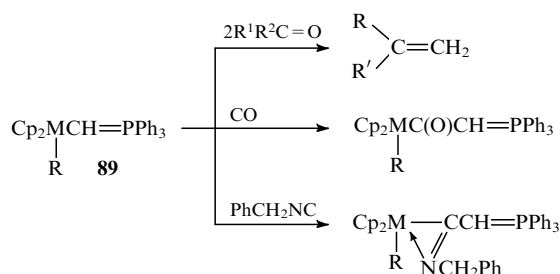


M = Ti, Zr, Hf.

When bis(cyclopentadienyl) diphenylzirconium was heated with triphenylphosphonium ethylide, the cyclic metallocene ylide **90** was formed as a result of *ortho*-metallation of the benzene ring.^{161, 162}



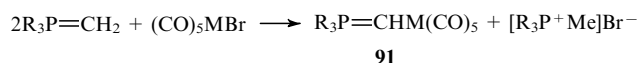
The nucleophilicity of the metallocene ylides **89** is lowered because of the high electron-acceptor ability of the transition metals.¹⁶¹ Nevertheless, the metallocene ylides **89** react with ketones.¹²⁵ Carbon monoxide and isocyanides readily insert into the zirconium–carbon bond of ylides **89**.^{160–165}



M = Ti, Zr, Hf.

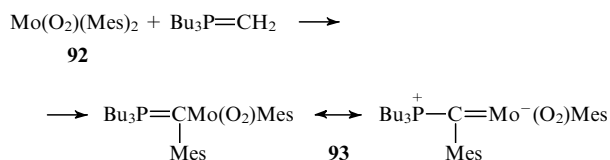
4. Ylides containing the Group VIB–VIII metal atoms

Phosphorus ylides containing atoms of Group VI–VIII transition metals are characterised by high stability on storage and the ability to exist in a free, non-associated form. Recent detailed studies of the phosphorus-ylide complexes of Group VI–VIII transition metals allowed convenient procedures for their synthesis to be elaborated. The simplest method involves the substitution of ligands in the transition metal complexes by the phosphorus-ylide ligand.^{158, 166–174} For instance, bromopentacarbonyl complexes of manganese and rhenium undergo transylidation with phosphorus ylides to give the C-metal-substituted phosphorus ylides **91**.^{158, 166}

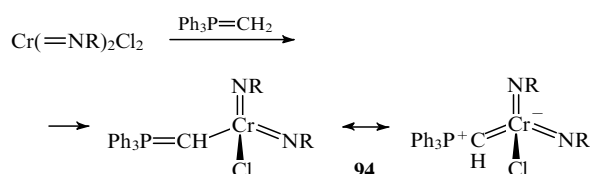


M = Mn, Re.

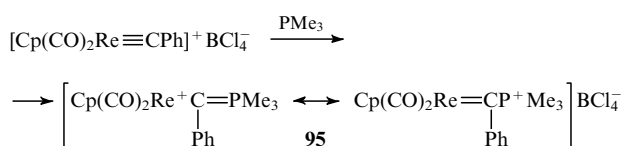
The dioxomolybdenum ylide **93** was synthesised by the reaction of the dioxomolybdenum complex **92** with tributylphosphonium methyllide.^{168, 169}



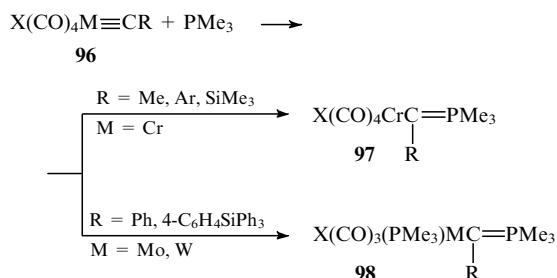
The first complex of hexavalent chromium **94**, which has high reactivity, was synthesised by the transylidation reaction of a bisalkylimide chromium complex with 2 equivalents of triphenylphosphonium methyllide.¹⁷⁰



The phosphorus ylide **95** was synthesised by addition of trimethylphosphine to a cationic rhenium complex. The bond between the rhenium atom and the ylide carbon atom in compound **95** is shortened because of the effective delocalisation of the negative charge on the ylide carbon atom by the transition metal.^{171–178}

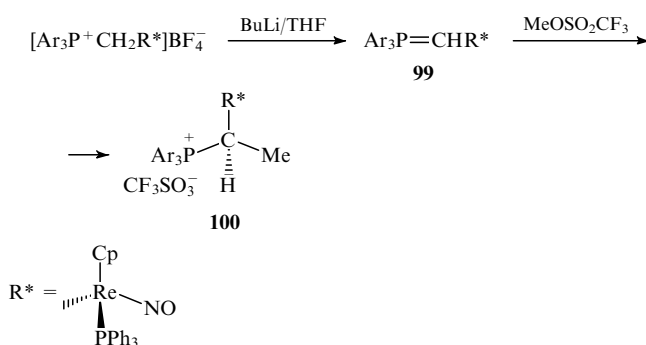


Tertiary phosphines add to chromium, molybdenum, and tungsten carbyne complexes even at -60°C to form stable metal-substituted phosphorus ylides **97** and **98**.^{171, 172}

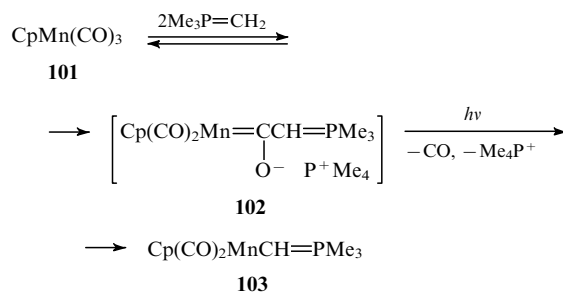


X = Cl, Br, I.

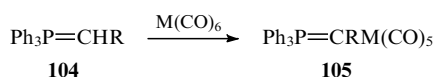
The phosphorus ylides containing Group VI–VIII elements at the α -carbon atom may be obtained by the salt method.^{173, 179} This method was used to prepare optically active phosphorus ylides **99** with a chiral rhenium atom, their treatment with methyl triflate in THF at -78°C produced the (*S,S,R,R*)- α -rhenium-substituted phosphonium salt **100**¹⁶⁶ as a result of asymmetric induction at the α -carbon atom.



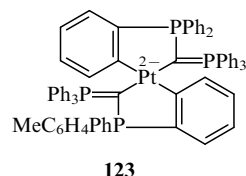
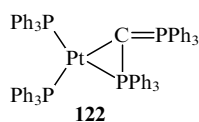
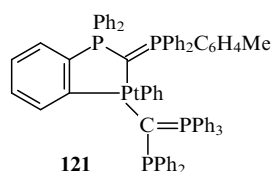
The manganese complex **101** reacts with trimethylphosphonium methyllide to give the mesomeric, anionic manganese-substituted phosphorus ylide **102** as the adduct which is in equilibrium with the starting compound. Photolysis of the compound **102** occurs with the elimination of carbon monoxide and results in a neutral ylide **103** with a manganese atom at the α -carbon atom.^{180–183}



The phosphorus ylides react with the ligands of transition metal complexes to give C-metal-substituted phosphorus ylides.^{184–187} For instance, when chromium, molybdenum and tungsten hexacarbonyls were heated with ylides **104** at $50\text{--}60^\circ\text{C}$ in light petroleum or were subjected to UV irradiation, complexes **105** were obtained.^{188–191}



R = Ph, CH=CH₂, CH₂CH=CH₂, CH₂CMe=CH₂,
CH=CHMe, CH=CHPh; M = Mo, W.



* * *

It follows from the above material that transition metals effectively stabilise the ylide carbanion lowering its nucleophilicity. Nevertheless, in some cases such ylides exhibit a relatively high reactivity. The phosphorus ylides containing transition metals have not yet found extensive application in synthesis. Certain prerequisites allow one to anticipate considerable extension of their practical application. For instance, the metal complexes of phosphorus ylides are reported to be used as catalysts for the polymerisation of alkenes and as medicinals.^{214–216}

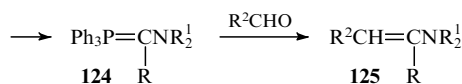
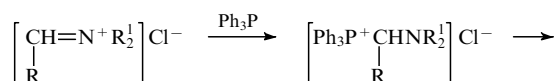
IV. Phosphorus ylides substituted at the α -carbon atom by atoms of elements of Groups VA – VIIA of the Periodic Table

The phosphorus ylides substituted by Group VA – VIIA elements at the α -carbon atom are of both theoretical and synthetical interest. They are widely used in the synthesis of biologically active compounds.^{9, 217–220}

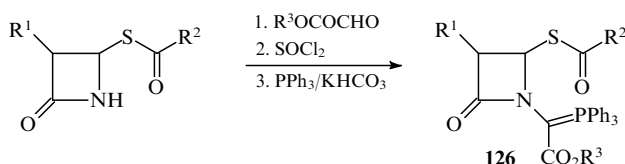
1. Ylides containing the Group VA elements

The structures of the phosphorus ylides stabilised by nitrogen, phosphorus, and arsenic atoms are highly diversified due to the varying valence and different coordination states of these elements. The chemical properties of such phosphorus ylides are also characterised by considerable peculiarities. All this promoted the development of the chemistry of this class of phosphorus ylides and elaboration on their basis of new preparative methods for the synthesis of various valuable organic compounds.

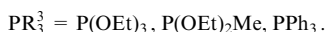
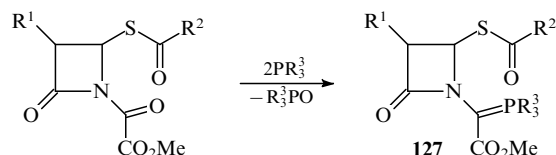
Quantum-chemical *ab initio* calculations¹¹⁶ show that the trivalent nitrogen atom destabilises the ylide carbanion. Therefore, the C-amino-substituted phosphorus ylides are stable only if the second substituent at the α -carbon atom exhibits electron-accepting properties, which compensate the electron-donating effect of the amino group. For this reason, the transylidation reaction cannot be used for the synthesis of C-amino-substituted ylides. The C–N-ylides are usually synthesised by the dehydrohalogenation of the corresponding phosphonium salts. The Wittig reaction of the C–N-ylides **124** generated from the C-amino-phosphonium salts leads to the enamines **125**. Attempts to synthesise the non-stabilised C–N-ylides have failed.²²¹



The reactions developed by Woodward²²² for the synthesis of the ylides **126** containing the 4-acylthioazetidin-2-one group at the α -carbon atom, which are used for the preparation of the β -lactame antibiotics, are of considerable preparative value.

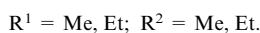
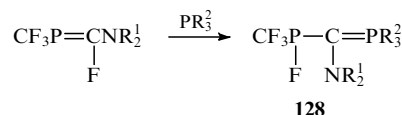


A method of generation of the phosphorus ylides based on the reaction of azetidine derivatives with an excess of a phosphite, phosphinite, or tertiary phosphine gained industrial significance.^{218, 219} The reaction is carried out at room temperature under mild conditions.²²⁰

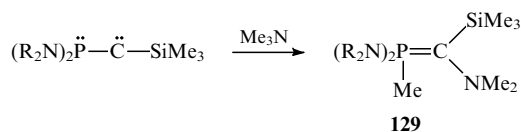


The phosphorus ylides **127**, that are formed with high yield readily enter into the Wittig reaction.

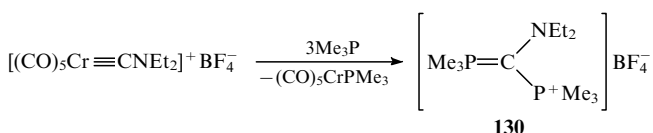
The reaction of the compounds of two-coordinate phosphorus with lower trialkylphosphines leads to the phosphorus ylides **128**, which contain a phosphorus atom and a dialkylamino group at the α -carbon atom. This reaction is accompanied by the substitution of the fluorine atom at the sp^2 -hybridised carbon atom with the phosphonium group and substituent migration of the fluorine atom to the trivalent phosphorus atom.²²³



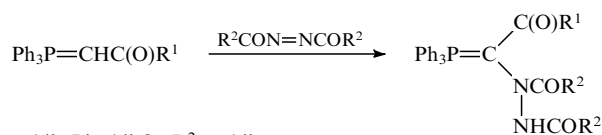
Cowley *et al.*²²⁴ have synthesised the C–N-phosphorus ylide **129** by adding trimethylamine to a phosphinocarbene.



Kreissl *et al.*²²⁵ have synthesised the ylide-phosphonium salt **130** by the reaction of trimethylphosphine with a carbene–chromium complex.

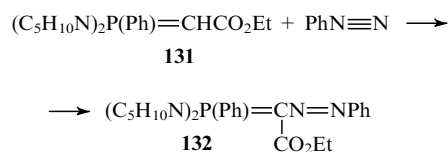


The Michael addition of phosphorus acyl ylides to cyclic and acyclic compounds with a multiple N=N bond activated by carbonyl groups is a convenient way for the synthesis of C–N ylides.^{226–228}



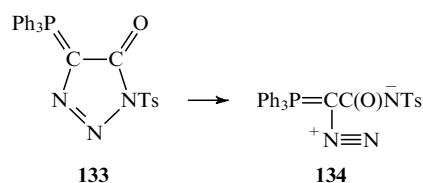
$\text{R}^1 = \text{Alk}, \text{Ph}, \text{AlkO}; \text{R}^2 = \text{Alk}.$

Triphenylphosphine and phosphorous acid amides react with C-ethoxycarbonyl- and C-acetyl-N-nitrile imines to give stable azomethylenephosphonium ylides $\text{R}_3^1\text{P}=\text{C}(\text{R}^2)\text{N}=\text{NPh}$ [$\text{R}^1 = \text{Ph}, \text{C}_5\text{H}_{10}\text{N}; \text{R}^2 = \text{CO}_2\text{Et}, \text{C}(\text{O})\text{Me}$].^{229, 230} The ylide **132** has been obtained by the reaction of the ylide **131** with diazonium salt followed by the treatment with sodium ethoxide.²³¹



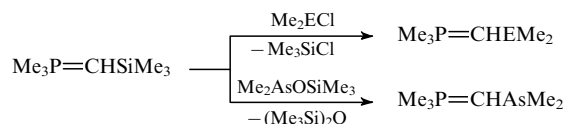
The ylide $\text{Ph}_3\text{P}=\text{C}(\text{N}=\text{NPh})_2$ with the two azogroups at the α -carbon atom has been prepared by reaction of bisphenylazomethane with triphenyldichlorophosphorane in the presence of triethylamine.²³²

The 1,3-dipolar cycloaddition of triphenylphosphonium ketene ylides to toluenesulfonyl azide leads to the ylides **133** containing a triazoline ring, which may produce ylides **134** with a diazo group at the α -carbon atom.²³³

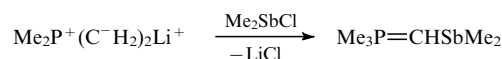


In contrast to the nitrogen atom, the atoms of trivalent phosphorus, arsenic, and antimony efficiently stabilise the ylide carbanion, thus making the transylidation reaction the main route to the synthesis of C-phosphino-, C-arsino-, and C-stibino-substituted phosphorus ylides.^{79, 80}

These ylides are obtained by the reaction of C-silyl- and C-lithium-substituted phosphorus ylides with chlorophosphines, -arsines, and -stibines.

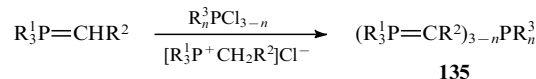


$\text{E} = \text{P}, \text{As}, \text{Sb}.$



Trimethylsilyl arsinic acid may be used instead of chloroarsines.^{79, 80, 154}

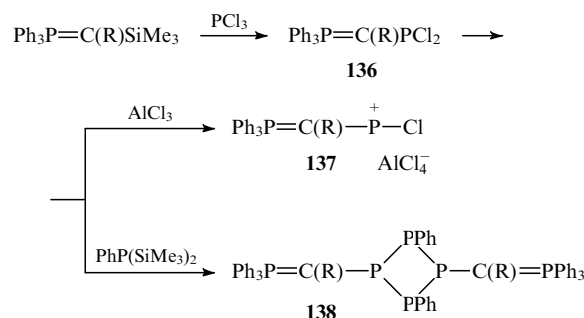
Diaryl- and dialkyl-chlorophosphines, alkyl- and aryl-chlorophosphines, aminochlorophosphines, and phosphorus trichloride react with non-stabilised phosphorus ylides to give the compounds **135** with one, two, or three phosphorus ylide groups at the trivalent phosphorus atom.^{156, 234–238}



135

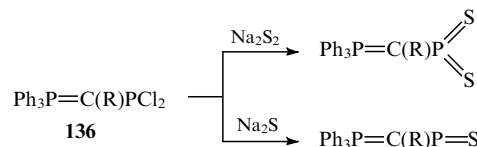
$\text{R}^1 = \text{Ph}, \text{Alk}_2\text{N}; \text{R}^2 = \text{H}, \text{Alk}; \text{R}^3 = \text{Alk}, \text{Ar}, \text{Alk}_2\text{N}, \text{Cl};$
 $n = 0-2.$

Schmidbauer *et al.*^{239, 240} have synthesised the dichlorophosphinoylide **136**, which is an interesting initial compound for preparation of phosphorus ylides of unusual structure. In the reaction with aluminium chloride, it gives the ylidylphosphonium cation **137** and with bis(trimethylsilyl)phenylphosphine it gives 1,3-bis(triphenylphosphoniumylidyl)cyclotetraphosphine **138**. X-Ray structural analysis of the compound **138** demonstrated *trans*-orientation of all the substituents of the four-membered ring.²⁴¹

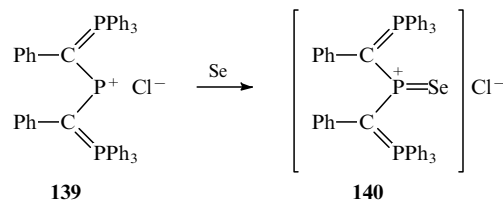


$\text{R} = \text{Alk}, \text{Ar}, \text{SiMe}_3.$

Dichlorophosphinoylide **136** was used by Schmidpeter *et al.* for the synthesis of the first stable phosphorus ylides with the phosphorus sulfide and phosphorus disulfide groups at the ylide carbon atom.^{242–244}



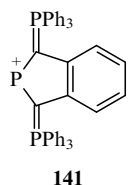
In the last few years, considerable attention has been paid to the synthesis of phosphorus ylides substituted at the ylide carbanion with phosphorus atoms with unusual coordination.^{242–248} Phosphorus ylides, which contain two-coordinate trivalent^{242, 248} and three-coordinate pentavalent phosphorus atoms^{243, 244} at the ylide carbon atom have been synthesised. Schmidpeter^{244, 245} has shown that bisylide-substituted monochlorophosphine **139** with the phosphonium structure adds selenium with the formation of bisylide-substituted selenoxophosphonium chloride **140**. The compound **140** was the first chalcogen-phosphonium ion with a trigonal planar phosphorus atom isolated in the individual form.^{244, 245}



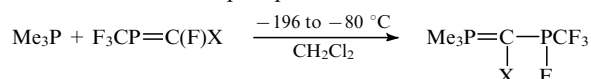
139

140

Diphosphoniumisophosphindol **141** containing a two-coordinate phosphorus atom at the ylide carbon atom has been synthesised by the reaction of the corresponding bisphosphorane with phosphorus trichloride and triethylamine.^{243, 245, 246} The crystal and molecular structure of the phosphorus ylide **141** was described.^{245, 249}

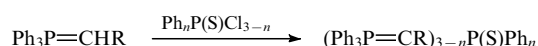


Grobe *et al.*²⁴⁷ have prepared phosphorus ylides substituted with the trivalent phosphorus atom at the ylide carbon atom by adding trimethylphosphine to fluorinated phosphaaalkenes. The formation of the ylides was explained by the electrophilic character of the two-coordinate phosphorus atom.



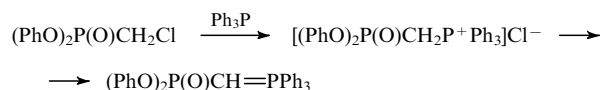
X = F, OMe, OEt.

The four-coordinate phosphorus atom efficiently stabilises the ylide carbanion, which makes the reaction of transylidation the general technique for the preparation of various C-phosphorus-substituted ylides containing phosphoryl or thiophosphoryl groups at the α -carbon atom.^{117, 209, 250} This method has also been used for the synthesis of ylides containing one, two, or three P=C groups at the four-coordinate phosphorus atom.^{154, 238, 251}

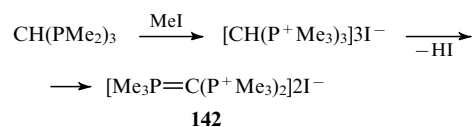


$n = 0-2$.

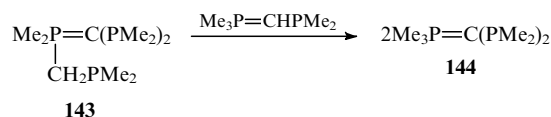
The salt method has also been used, although not so often, for the preparation of the C-phosphorus-substituted ylides. Thus triphenylphosphonium diphenylphosphonemethylide can be obtained by the quaternization of triphenylphosphine with diphenyl chloromethylphosphonate on heating to 175 °C.²⁵²



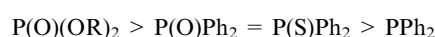
The bis- and tris(diorganylphosphino)methanes are alkylated by alkyl halides with the formation of the methylenephosphonium salts, which give carbodiphosphoranes²⁵³ on dehydrohalogenation. Similarly, tris(diorganylphosphino)methanes give ylide-bisphosphonium salts **142**.²⁵³⁻²⁵⁹



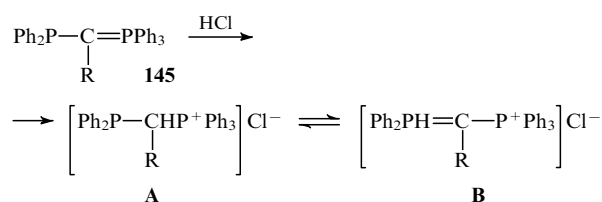
The ylide **143** (for the synthesis of the ylide **143** see Refs 255-264) easily undergoes recombination with trimethylphosphonium dimethylphosphinomethylide to give the bisphosphino-substituted ylide **144**.^{74, 151, 254, 255}



The phosphorus ylides stabilised by phosphorus, arsenic or antimony atoms are thermally stable. Tri- and penta-valent phosphorus atoms at the ylide carbon atom efficiently delocalise its electron density, which is confirmed by physicochemical studies.^{251, 265} Thus the effect of the phosphorus-containing groups X on the CH-acidity of the ylides $\text{Ph}_3\text{P}=\text{CHX}$ forms the following series:

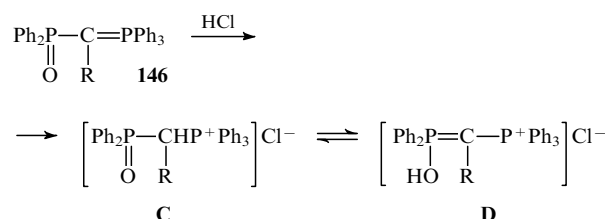


X-Ray structural studies of the element-substituted phosphorus ylides reveal the shortening of the P=C bond (in Å): $\text{Ph}_3\text{P}=\text{C}(\text{R})\text{EPh}_2$: 1.720 (E = P),²⁶⁶ 1.698 (E = As),²⁶⁷ and 1.692 (E = Sb).²⁶⁸ Two or three phosphonium groups at the ylide carbon atom decrease even more the basicity of the compounds.^{269, 270} For instance, tris(triphenylphosphonium) methylide cannot be protonated even by strong acids. Bis(triphenylphosphonium) diphenylphosphinomethylide **145** (R = P^+Ph_3) is protonated at the trivalent phosphorus atom,^{215, 216} while triphenylphosphonium diphenylphosphino(e-thoxycarbonyl)methylide (R = CO_2Et) is protonated both at the α -carbon atom and at the trivalent phosphorus atom.²⁷¹ Mastryukova *et al.*²⁷² have shown by NMR the existence of a tautomeric equilibrium between the A and B forms of the compound **145**.

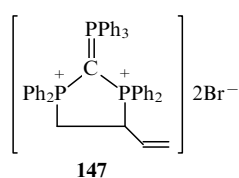


R = CO_2Et .

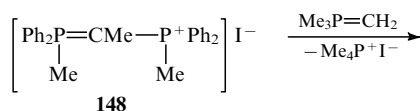
The protonation of the phenylphosphinoyl methylide **146** leads to CH- (C), or OH-protonated (D) forms depending on the properties of the substituents R. Protonation at the carbon atom takes place in the case of R = $\text{SO}_2\text{C}_6\text{H}_4\text{Me}$ -4 and PPh_3 . If R = CO_2Et the OH- and CH-protonated forms coexist in solution in a tautomeric equilibrium.²⁷³

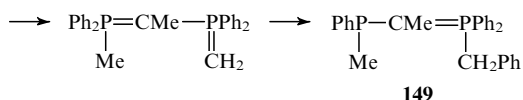


The alkylation of the phosphine-phosphonium ylides occurs at the trivalent phosphorus atom with the formation of P-alkylated phosphonium salts, while the alkylation of the phosphoryl- or thiophosphoryl-substituted phosphorus ylides gives the C-substituted phosphonium salts.^{251, 265, 274} The reaction of triphenylphosphonium bis(diphenylphosphino)methylide with 1,4-dibromobut-2-ene is a convenient method for the preparation of the ylide-phosphonium salts **147** containing the 1,3-diphospholane ring.^{275, 276}



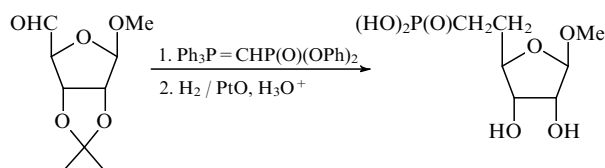
Some C-phosphorus-containing phosphorus ylides undergo skeletal rearrangements. Under the action of the trimethylphosphonium methylide, the phenyl group migrates from the phosphorus atom to the ylide carbon atom, and the phosphonium salt **148** is converted into the phosphorus ylide **149**.²⁷⁷



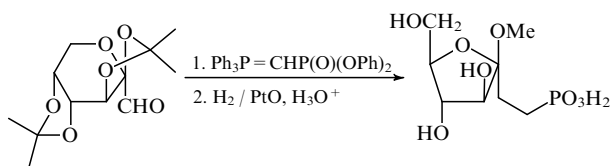


Despite the relatively low nucleophilicity of ylides stabilised by the four-coordinate phosphorus atom, they enter into the Wittig reaction with aldehydes on heating to form phosphorus-containing alkenes. The use of *C*-phosphorus-substituted ylides as alkenating agents is especially important for the synthesis of natural substances. In particular, the *C*-phosphorus-substituted ylides are used to prepare isosteric analogues of phosphates of natural origin.^{278–280}

Carbohydrates with protected hydroxy groups are easily alkenated by triphenylphosphonium diphenoxyphosphorylmethylide. The vinylphosphonates formed as a result of the alkenation are hydrogenated over platinum or palladium oxide and hydrolysed to form the phosphonic acids.²⁸¹

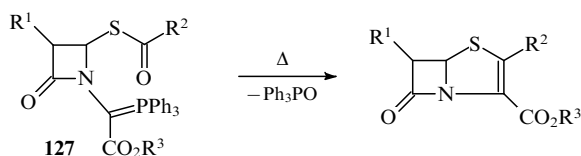


Using the same triphenylphosphonium diphenoxyphosphorylmethylide, the synthesis of the phosphonate analogue of fructose-1-phosphate has been performed; this manifested the properties of bioregulator of hexose-phosphate transport systems.²⁸²

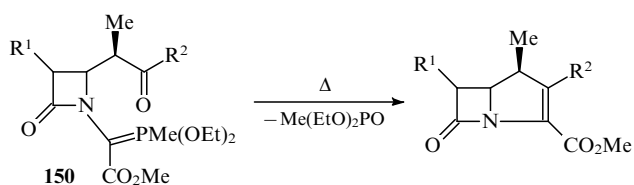


Similarly, isosteric analogues of a series of phospholipids and sugar phosphates have been prepared.^{283–285} Huang *et al.*²⁸⁶ have synthesised phosphorus-containing pyrethroids using *C*-phosphorus-substituted ylides.

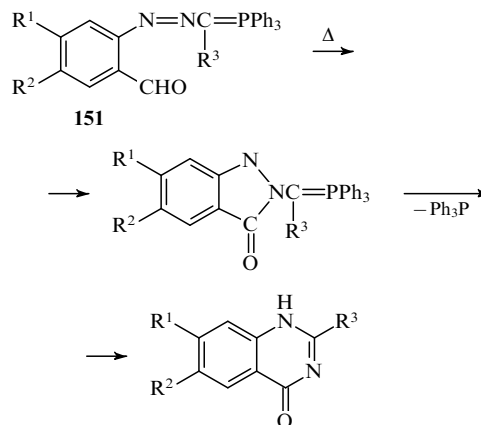
The phosphorus ylides **127** undergo an intramolecular Wittig reaction on heating and give penemates in high yields. They have found an important practical application in the synthesis of β -lactam antibiotics.²⁸⁷ Syntheses of a series of other β -lactam antibiotics, which are derivatives of penem and cefemic acids, have been described.^{287–295}



Japanese workers have prepared carbopeneme derivatives in high yields by refluxing the phosphorus ylide **150** in xylene. This technique has been proposed for industrial application.^{218, 219}

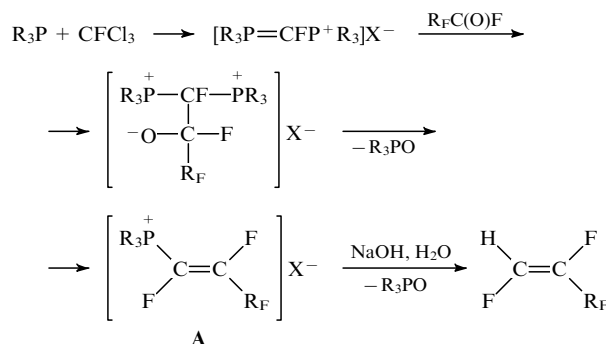


The thermolysis of triphenylphosphonium azomethylide gives the ylides **151** which are converted into 4-oxo-1,4-dihydroquinazolines on further heating.^{227, 296, 297}

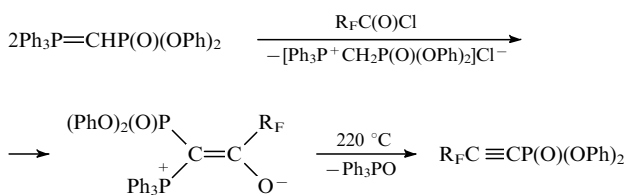


$\text{R}^3 = \text{CO}_2\text{Me}, \text{C}(\text{O})\text{Me}, \text{SO}_2\text{Ph}, \text{SO}_2\text{C}_6\text{H}_4\text{Me-4}, \text{C}(\text{S})\text{SMe}.$

Burton *et al.* have developed a method for the synthesis of fluoroalkenes based on *C*-phosphorus-substituted ylides. The reaction presumably proceeds via a mechanism similar to that of the Wittig reaction and involves the formation of a betaine, which decomposes to give phosphine oxide and vinylphosphonium salt **A**. The phosphonium salt **A** readily decomposes with the cleavage of the C–P bond under the action of dilute alkali. The yields of fluoroalkenes do not exceed 45%–62%.^{298, 299}

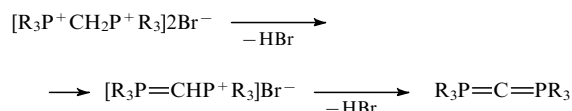


Perfluoroalk-1-ynylphosphonates are obtained by pyrolysis of 2-hydroxyalkenyltriphenylphosphonium ylides, which follows the intramolecular Wittig-type reaction.³⁰⁰

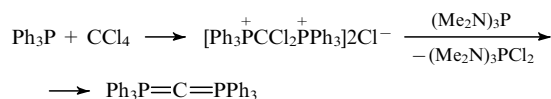


C-Phosphine-substituted phosphorus ylides are used as ligands in transition metal complexes.^{226, 260–264} Thus substitution of the ligands in the chromium carbonyl complexes $\text{Cr}(\text{CO})_5\text{L}$, where $\text{L} = \text{THF}, \text{C}_7\text{H}_8, \text{Me}_2\text{S}(\text{O})\text{CH}_2$ by *C*-phosphine-substituted phosphorus ylides leads to cyclic and acyclic phosphorus ylides with a metal–phosphorus(III) bond. These complexes are diamagnetic substances stable in air and soluble in organic solvents.^{184, 301}

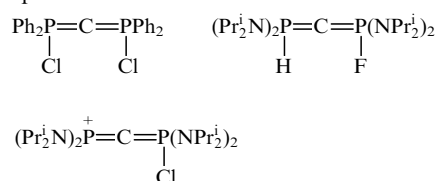
Carbodiphosphorane dicarbanions stabilised by two phosphonium groups provide an example of *C*-phosphorus-substituted ylides important for synthesis.³⁰² Carbodiphosphoranes are obtained by dehydrohalogenation of the ylide-phosphonium salts with sodium amide, butyllithium, potassium in dimethoxyethane, sodium hydride, triethylphosphonium ethylide.^{303–308}



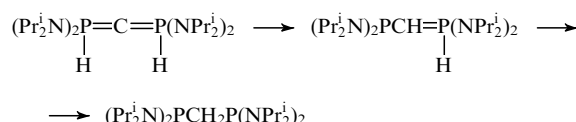
The ylide-phosphonium salts formed upon the treatment of triphenylphosphine with carbon tetrachloride are dehydrochlorinated by tris-(dimethylamino)phosphine to give carbodiphosphoranes in good yields.³⁰⁵



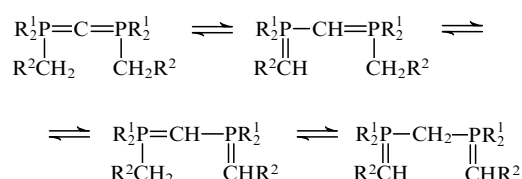
In the last few years, carbodiphosphoranes of unusual structure with fluorine, chlorine or even hydrogen atoms at the phosphorus atom have been obtained.^{309–313}



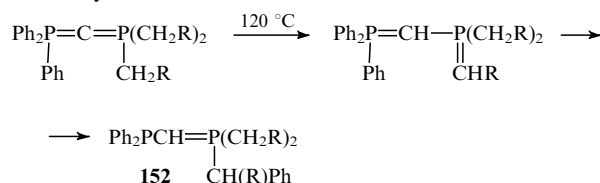
Carbodiphosphoranes $(\text{Pr}_2^i\text{N})_2\text{HP}=\text{C}=\text{PH}(\text{NPr}_2^i)_2$ with the P–H bond are unstable and are converted into aminophosphines as a result of a prototropic shift.^{10, 271, 313}



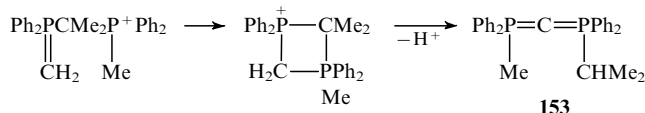
A close chemical interrelation exists between the carbodiphosphoranes and the C-phosphorus-substituted ylides. For instance, the carbodiphosphoranes with alkyl groups at the phosphorus atom exist as prototropic tautomers.^{314, 315} The tautomeric equilibrium depends on the electronic effect of the substituents. Electron-accepting and electron-donating substituents shift the equilibrium towards the bis-ylide or the carbodiphosphorane form, respectively. It is believed that the prototropic exchange between the tautomers is intramolecular.^{308, 314–318}



The asymmetric alkyl-containing carbodiphosphoranes are converted into phosphino-substituted ylides **152** on heating to 120 °C. The reaction occurs *via* intermediate formation of the bis-ylide as a result of phenyl group migration from the phosphorus atom to the ylide carbon atom.^{222, 319}

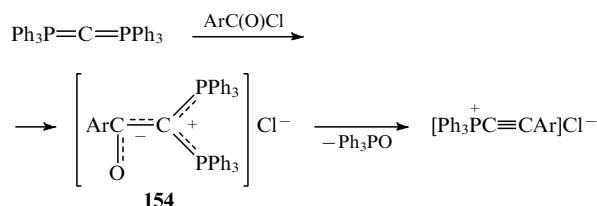


The ylide-phosphonium salts with a dimethylmethylene group between two phosphorus atoms undergo isomerisation *via* the four-membered intermediate state into the carbodiphosphoranes **153**.³²⁰

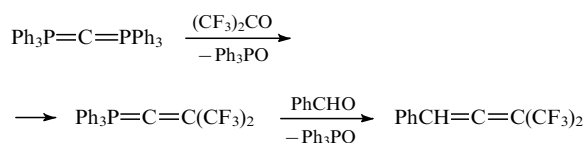


153

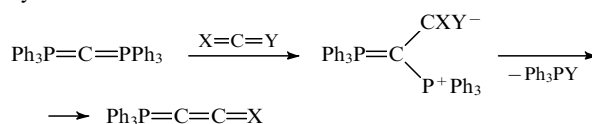
The reaction of carbodiphosphoranes with electrophiles results in substitution at the central carbon atom or in the side chain. For instance, hexamethylcarbodiphosphorane reacts with chlorotrimethylsilane to give the ylide containing a trimethylsilyl group at the side carbon atom. In contrast, reaction of carbodiphosphoranes with alkyl halides, chlorophosphines, and acid chlorides usually occurs at the ylide carbon atom with the formation of the corresponding ylide-phosphonium salts.²⁵⁹ In the reaction with aromatic acid chlorides, hexaphenylcarbodiphosphorane gives C-acylated ylide-phosphonium salts **154**, which are converted on heating into (arylethynyl)phosphonium salts as a result of an intramolecular Wittig reaction.³²¹



The carbodiphosphoranes are valuable reagents in organic synthesis. They exhibit high nucleophilicity and therefore readily react with aldehydes and ketones. The allenylides thus formed enter into the Wittig reaction with aldehydes and ketones to give allenes.²⁶²

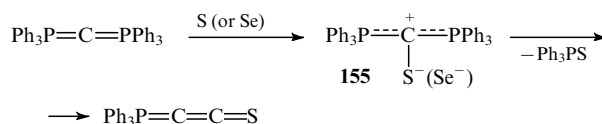


The reaction of carbodiphosphoranes with heterocumulenes (carbon dioxide, carbon disulfide, isocyanates, ketenes) yields betaines stable at room temperature, which are converted into phosphonium ketenylides, thioketenylides, keteniminylides, allenylides.^{304, 322–326}

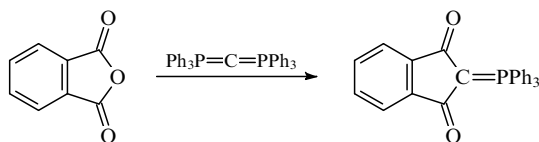


X = O, S, NAr, CPh₂; Y = O, S.

Hexaphenylcarbodiphosphorane when treated with sulfur or selenium first yields the betaines **155**, which are stable at low temperature; at room temperature, they are converted into the triphenylphosphonium ketenylides.³²⁷



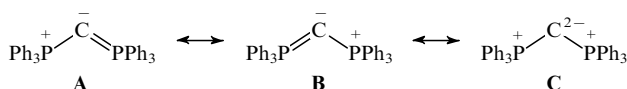
The reaction of hexaphenylcarbodiphosphorane with phthalic anhydride occurs with the substitution of the anhydride oxygen atom by the ylide function.^{321, 328}



In the reaction with salicyl aldehyde, hexaphenylcarbodiphosphorane gives a six-membered cyclic oxaphosphorane.³²⁹

Carbodiphosphoranes are used as ligands in ylide complexes of transition metals.^{135, 187, 330–335}

X-ray structural analysis and electron diffraction data proved carbodiphosphoranes to be dicarbanions. The central carbon atom of the carbodiphosphoranes has a hybridisation close to sp^2 , and the ground state of the carbodiphosphoranes may be described by the canonical structures **A**, **B**, and **C**.^{330–340}

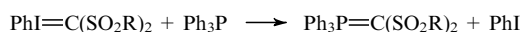
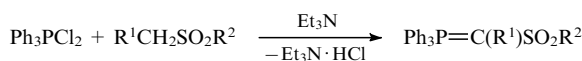


Structural investigations of hexaphenylcarbodiphosphorane with triboluminescent properties, *i.e.* the ability to generate light on mechanical treatment, are of special interest.^{340–343} Hexaphenylcarbodiphosphorane forms several crystalline modifications: orthorhombic crystals do not have triboluminescent properties, whereas monoclinic crystals do possess such properties. The molecules in monoclinic and orthorhombic modifications have different $P=C=P$ bond angles and $Ph-P\dots P-Ph$ dihedral angles.^{344, 345} The dipole moment of hexaphenylcarbodiphosphorane in benzene is 4.69 ± 0.05 D.^{337, 338}

2. Phosphorus ylides containing Group VIA elements

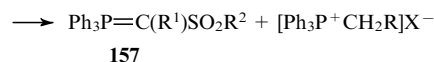
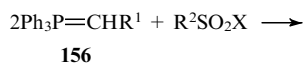
The phosphorus ylides stabilised by oxygen, sulfur, selenium or tellurium atoms possess diversified structures and properties. The chemistry of these ylides is being rapidly developed. Convenient procedures for their preparation are elaborated, and chemical properties are studied. The ylides stabilised by the Group VIA elements are used in the synthesis of natural substances and biologically active compounds.

The very stable *C*-sulfonyl-substituted ylides are the most readily available phosphorus ylides of this group. They can be prepared by simple methods, such as the direct phosphorylation of sulfonylalkanes by polyhalophosphoranes in the presence of triethylamine,³⁴⁶ the salt method in the presence of organic bases, or by the reaction of diphenyldialkylaminophosphines with bis(sulfonyl)methanes and alkyl halides.^{347–349} Heating of phenyliodonium ylides with triphenylphosphine in benzene in the presence of copper acetylacetonate as a catalyst gives phosphonium ylides in high yield.^{350, 351}

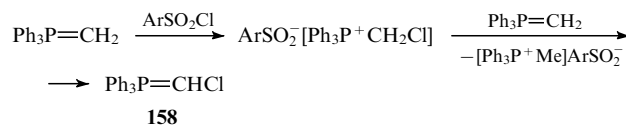


$R^1 = Me, Ph, SO_2R^2$.

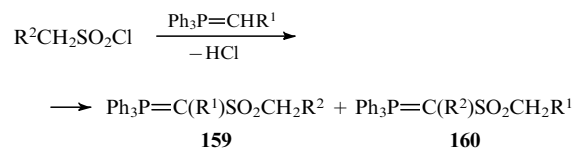
The sulfonyl ylides **157** can be obtained by the transylidation of phosphorus ylides **156** with sulfonyl fluorides or sulfonic anhydrides.^{348, 349} At the same time, the reaction of phosphorus ylides with arenesulfonyl chlorides results in the chloro-substituted phosphorus ylides **158** rather than the sulfonyl-substituted ylides.³⁴⁸



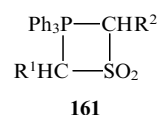
$X = F, R^3SO_3$;



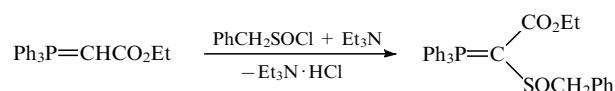
The reactions of phosphorus ylides with alkenesulfonyl halides are also accompanied by rearrangements, which result in migration of the substituent R^1 from the ylide carbon atom to the carbon atom of the SO_2CH_2 group sulfur atom and the substituent R^2 migrates to the ylide carbon atom. The ratio of the isomers of *C*-sulfonyl-substituted phosphorus ylides **159**, and **160** thus formed depends on the nature of the substituents R^1 and R^2 .^{350, 351}



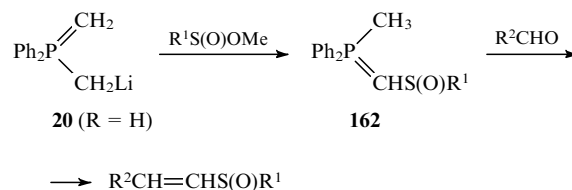
The reaction presumably proceeds *via* the formation of sulfenes $R^2CH=SO_2$, which give unstable four-membered cyclic intermediates **161** as a result of the addition to phosphoranes, and are subsequently converted into the isomers **159**, and **160**.



In order to introduce the sulfinyl group to the phosphorus atom, the reaction of the stabilised ylides with the sulfinyl chlorides in the presence of triethylamine is used. This reaction presumably proceeds *via* the intermediate formation of sulfines.^{352–354}

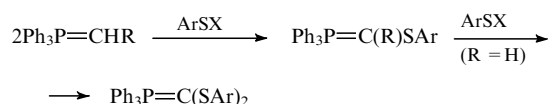


The reaction of diylides **20** ($R=H$) with sulfinates gives *C*-sulfinyl ylides **162**. The Wittig reaction of the latter with aldehydes proceeds with excellent stereoselectivity ($E:Z > 91:9$).



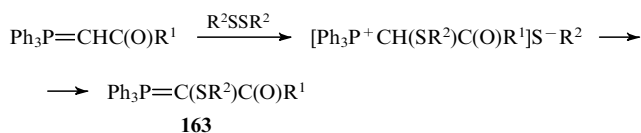
The same reaction with the chiral sulfinate yields chiral *E*-vinylsulfoxides ($E:Z > 99:1$) and is accompanied by the $>96\%$ inversion of configuration at the sulfur atom.⁵⁰

There exist convenient procedures for the preparation of the phosphorus ylides containing a bivalent sulfur atom at the α -carbon atom. The reactions of the stabilised and non-stabilised phosphorus ylides with sulfinyl chlorides in benzene or THF at $20^\circ C$ and the ratio of the reagents 2:1 or 3:1 are used most often. As a result of the transylidation reaction, the ylides containing one or two thio groups at the α -carbon atom are formed.^{354–358} Tolythio *p*-toluenesulfonate, *N*-methyl-*N*-phenylthioacetamide,¹⁶² dimethylsuccinimidiosulfonium chloride^{354, 355, 359} are used as thioaryllating reagents.



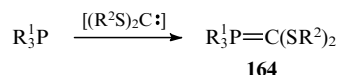
X = Cl, ArSO₂, MeC(O)NMe.

The reaction of phosphorus ylides with disulfides in benzene gives the ylides **163** in a yield of about 90%.^{354, 355, 360}



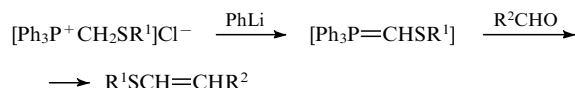
R¹ = Me, MeO; R² = R₂NC(S), EtO₂C.

The synthesis of the ylides **164** with two thioether groups at the carbon atom by the reaction of tertiary phosphines with bisalkyl(aryl)thiocarbenes has been reported.^{361, 362} Dithiocarbenes were generated by the action of sodium hydride on the corresponding tosylhydrazone³⁶¹ or by the decomposition of tris(phenylthio)methylithium.³⁶²

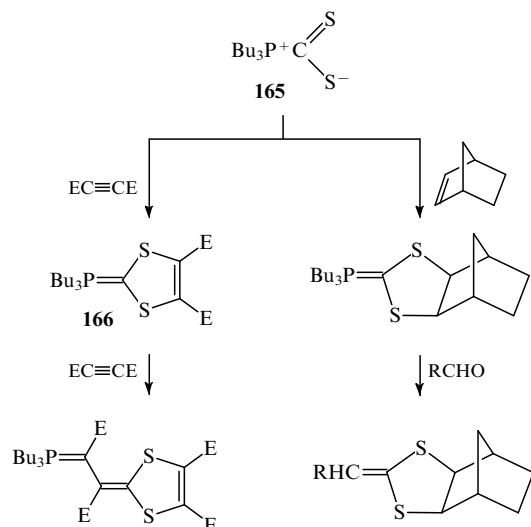


R¹ = Bu, Ph; R² = Et, Ph.

The most important method of synthesis of ylides containing alkylthio groups at the α-carbon atom is the dehydrohalogenation of the phosphonium salts by organolithium derivatives. The ylides synthesised by this method have been used in the Wittig reaction without isolation from the reaction solutions.^{8, 9}

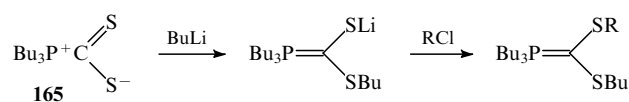


The adduct of tributylphosphine with carbon disulfide **165**, which was isolated more than a hundred years ago by Hoffmann,³⁶³ has been recently intensely studied. The ability of the adduct to enter into cycloaddition reactions with the formation of phosphorus ylides containing the dithiolane ring is not the least reason for such an interest.^{364, 365}



E = CO₂Et.

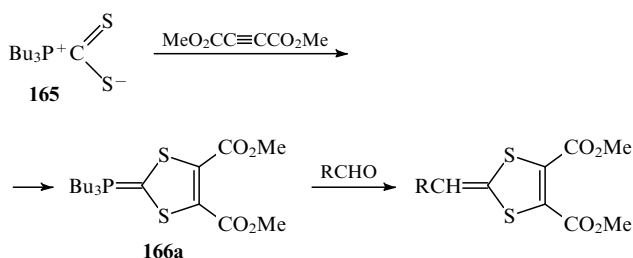
Polezhayeva *et al.* have introduced the adduct **165** into reactions with various dipolarophiles to prepare C-dithio-substituted phosphorus ylides of both cyclic and acyclic structure.³⁶⁶



R = Me₃Si, PhCH₂, Ph₂P.

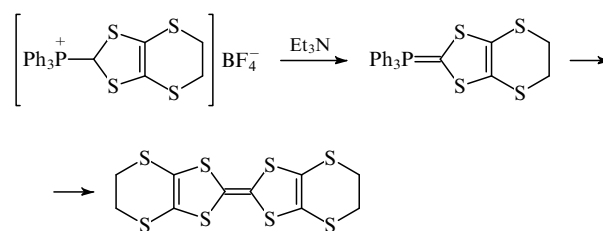
The ability of dithia- and tetrathiafulvenes to generate the electroconducting salts stimulated a great interest in phosphorus ylides containing thiafulvene groups.^{367–371} Thus 2-thioxo- and 2-oxo-1,3-dithiol-4-ylmethylides have been proposed as reagents for the synthesis of 1,3-dithia- and tetrathiafulvenes.³⁷²

The addition of dimethyl acetylenedicarboxylate to the adduct **165** has led to the highly reactive cyclic ylide **166a**, which enters into the Wittig reaction and yields dithiafulvenes with π-donating properties.³⁷⁰

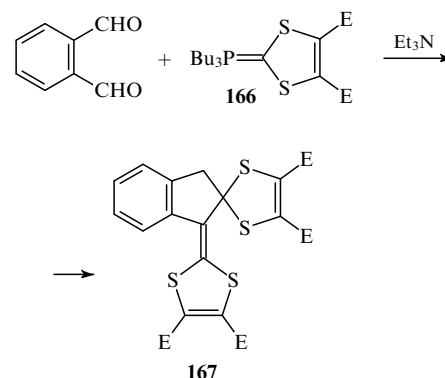


The 1,3-dithiol-2-ylides have been generated from the corresponding phosphonium salts with the dithiolane ring even under the action of triethylamine or diisopropylamine.³⁶⁷

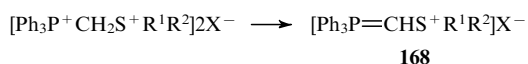
The ylides containing the 1,3-dithiol-2-ylide fragment have been used for the preparation of the corresponding polyformyltetrathiafulvalenes with a strong π-donating capacity.^{330, 369}



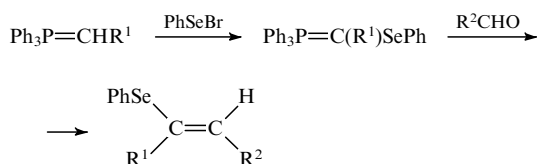
The derivatives of tetrathiafulvene **167** have been synthesised by the condensation of ylide **166** with phthalic aldehyde.³⁶⁸



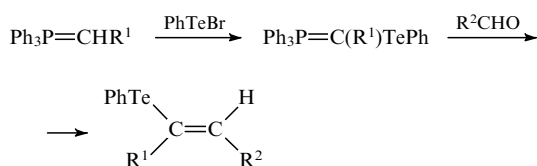
By the reaction of triphenylphosphonium methoxycarbonylmethylide with thiocyanogen, triphenylphosphonium 2-oxo-1-thiocyanopropylide, $\text{Ph}_3\text{P}=\text{C}(\text{SCN})\text{C(O)Me}$, has been synthesised in 65% yield.²⁹⁵ The alkylation of the alkylthiomethyltriphenylphosphonium salt gives the phosphonium sulfonium salt, which yields the ylide-sulfonium salt **168** upon dehydrohalogenation.³⁷³



It was proposed to prepare *C*-selenium-substituted ylides by the reaction of phosphorus ylides with phenylselenenyl bromide.³⁷⁴ The *C*-selenium substituted phosphorus ylides enter into the Wittig reaction with aldehydes to yield various phenylselenoalkenes.^{374–378}

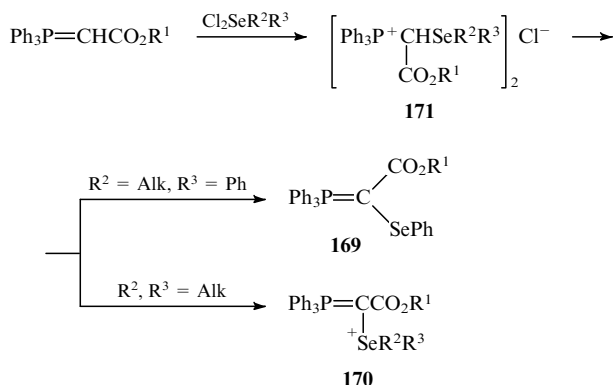


The *C*-tellurium-substituted phosphorus ylides have been synthesised similarly and used for the preparation of tellurium-substituted alkenes.³⁷⁹

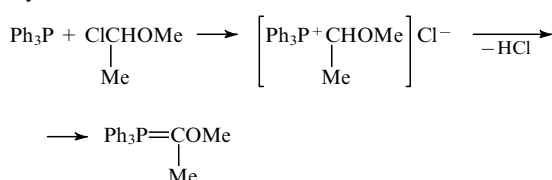


$\text{R}^1, \text{R}^2 = \text{Alk}, \text{Ar}$.

The reaction of dichloroselenides with triphenylphosphonium alkoxycarbonylmethylides results in the *C*-selenium-substituted ylides **169** or phosphonium selenonium ylides **170**. If the intermediate salts **171** contain two alkyl groups, they are dehydrochlorinated by the excess of phosphorus ylide with the formation of ylide-selenonium salts **170**. If there are a phenyl and an alkyl group at the selenium atom, the ylide **169** is formed.^{380, 381}



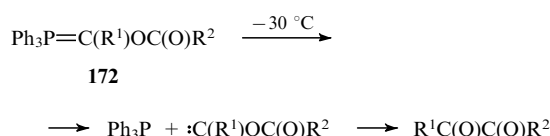
The phosphorus ylides with alkoxy and aroxy groups at the α -carbon atom are usually obtained by the salt method.^{383, 384} Thus the treatment of a suspension of a finely-ground phosphonium salt by phenyllithium in ether gives a bright-red solution of *C*-alkoxymethylide, which readily reacts with aldehydes and ketones to give alkyl vinyl ethers.^{365, 383} Triphenylphosphonium α -methoxyethylide is prepared by the reaction of triphenylphosphine with α -chloroethyl methyl ether in benzene. The phosphonium salt is then treated with potassium *tert*-butoxide in dimethoxyethane at -40°C for a few minutes. The red solution of the highly active ylide is formed which easily alkenates aldehydes and ketones.³⁸⁵



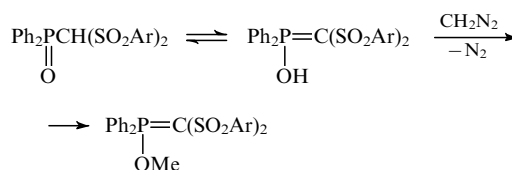
The ylides with oxygen or bivalent sulfur atoms at the α -carbon atom are unstable. They are normally used for the further one-pot chemical transformation. *ab initio* Calculations show that although the presence of the oxygen atom at the negatively charged carbon atom should in general stabilise the carbanion, it is not the case for the phosphorus ylides. *C*-Oxygen-substituted phosphorus ylides exhibit an enhanced tendency to dissociate into carbenes and tertiary phosphine, which allows one to regard them as the carbene complexes of tertiary phosphines. The formation of carbenes at the intermediate stage of the reaction is confirmed by *ab initio* calculations by the extended Huckel method in the 6-31 basis set.¹⁶



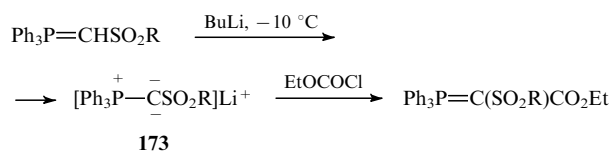
The ylides **172** also decompose readily with the formation of carbenes, which give 1,2-diketones as a result of intramolecular rearrangement.³⁸⁶



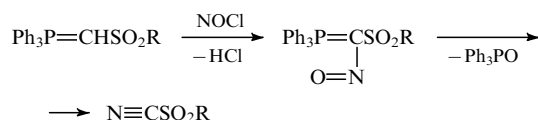
The *C*-Sulfonyl-substituted ylides are characterised by high thermal stability due to efficient delocalisation of the negative charge of the ylide carbon atom by the hexavalent sulfur atom, which has been confirmed by physicochemical studies,^{387–392} in particular by X-ray structural analysis.^{348, 393} The IR- spectra of ylides containing sulfonyl or sulfinyl groups at the carbon atom show considerable shift of the $\text{S}=\text{O}$ and SO_2 frequencies towards the longwave region due to the efficient delocalization of the carbanion negative charge by these groups.^{349, 387–390} The triad prototropic tautomerism is typical of bis(arylsulfonyl)methylphosphine oxides, which exist in the CH -phosphine oxide form in crystals and as tautomeric mixtures of the OH -ylide and CH -phosphine oxide forms in solutions; these forms can be easily indicated by spectroscopy.³⁹¹ Diphenylbis(arylsulfonyl)methylphosphine oxides resemble in their chemical properties the OH -acids of tetracoordinated phosphorus. Thus, they are *O*-methylated by diazomethane.^{391, 392}



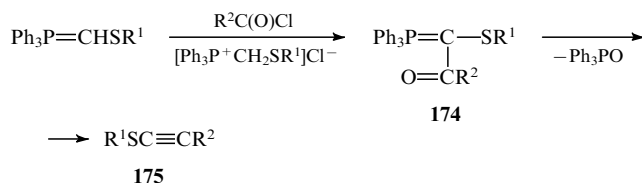
Hydrogen at the α -carbon atom in the *C*-sulfonyl-substituted ylides is active and can be readily substituted by various groups. The treatment of the ylides by butyllithium results in the substitution of the hydrogen atom by lithium with the formation of the dicarbanion **173**, which reacts with chlorine-containing electrophiles.³⁴⁸



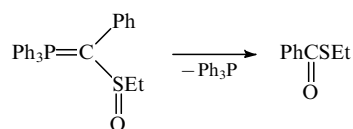
The reaction of *C*-sulfonyl-substituted ylides with nitrosyl chloride in pyridine leads to the substitution of the hydrogen atom at the α -carbon atom by a nitroso group. The ylide thus formed is converted into sulfonyl cyanide in a Wittig-type intramolecular reaction.^{348, 394}



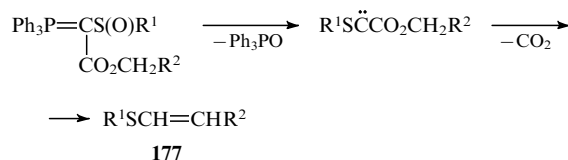
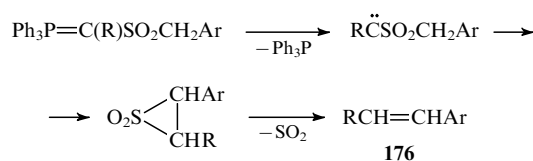
Flash-vacuum pyrolysis of the acylmethylides **174** obtained by the reaction of the C-alkylthio-substituted ylides with acid chlorides produces the alkyl(aryl) thioacetylenes **175** in good yields.^{348, 358, 394, 395}



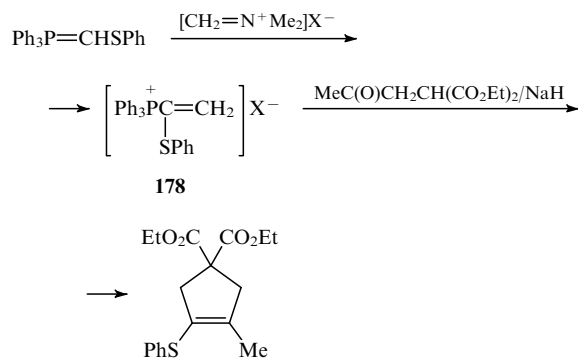
Flash-vacuum pyrolysis of sulfinyl-stabilised ylides gives thioesters in satisfactory yield.³⁹⁷



Flash-vacuum pyrolysis of sulfonyl- and sulfinyl-stabilised phosphorus ylides is accompanied by the elimination of phosphine or phosphine oxide with the formation of thio-, sulfinyl-, or sulfonylcarbenes, which give the alkenes **176** and **177** as a result of rearrangements and insertion reactions.^{396, 397}



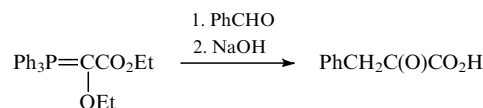
The substituted vinylphosphonium salts **178** are obtained by the reaction of phenylthiomethylides with iminium salts; they are used in the synthesis of cyclopentadienes.³⁹⁸



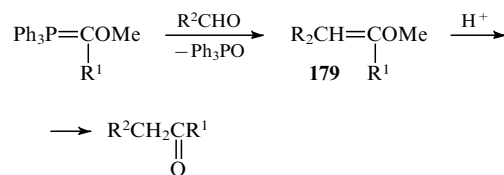
The C-sulfonyl-substituted ylides are characterised by weak basicity and nucleophilicity, which accounts for their low activity in the Wittig reaction. The monosubstituted ylides react only with aldehydes and do not react with ketones. Triphenylphosphonium bis-sulfonylmethylides also do not react with carbonyl com-

pounds. On the contrary, phosphorus ylides with alkylthio, alkoxyl, or aryloxy groups at the α -carbon atom readily enter into the Wittig reaction with various carbonyl compounds.^{399–410}

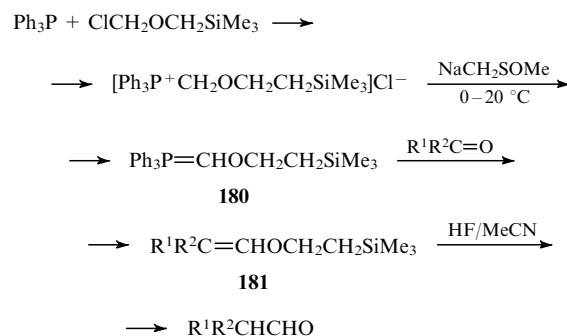
The reaction of ethoxy(ethoxycarbonyl)methylides with aldehydes and the subsequent hydrolysis of the vinyl ethers formed is a convenient way for the preparation of oxo carboxylic acids.⁴⁰³



The ylides with the alkoxyl groups at the ylide carbon atom alkenate both aldehydes and ketones with the formation of the vinyl ethers **179**, which give on hydrolysis the corresponding aldehydes ($\text{R}^1=\text{H}$) or ketones ($\text{R}^1=\text{Me}$), the latter may be again introduced into the Wittig reaction with triphenylphosphonium methoxymethylide thereby extending the carbon chain.^{399–401}

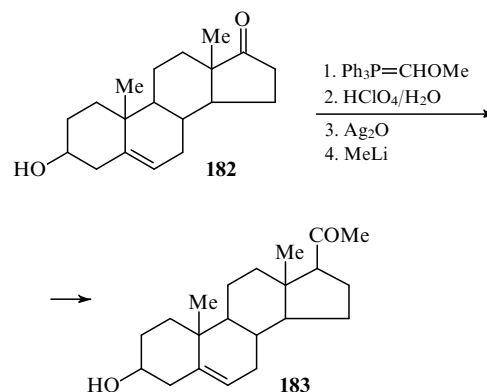


The silicon-containing α -alkoxymethylides **180** are especially convenient for this purpose. Vinyl ethers **181** that are formed in the reaction of the ylide **180** with aldehydes and ketones give aldehydes on treatment with 5% hydrogen fluoride in acetonitrile or with perchloric acid.



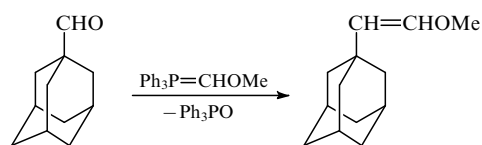
This method has been used for the preparation of various steroid aldehydes.^{401–410}

Danishefski *et al.* have developed a simple method for the preparation of pregnenolone **183** by the reaction of the androstenedione **182** with the C-oxygen-substituted ylide, prepared by dehydrohalogenation of the methoxymethyltriphenylphosphonium salt with sodium hydride in dimethyl sulfoxide.^{411, 412}

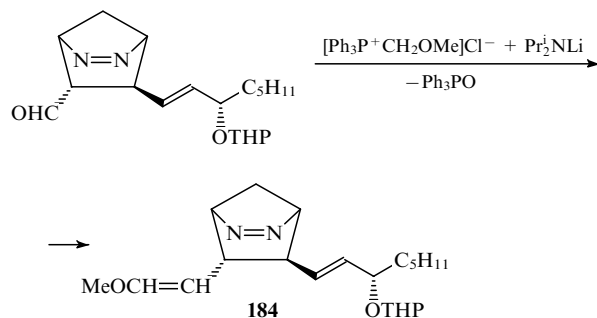


Triphenylphosphonium methoxymethylide enters into the Wittig reaction with sterically hindered carbonyl compounds.

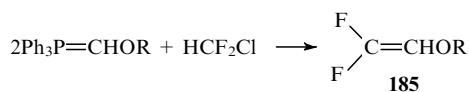
For instance, it easily alkenates adamantane-1-carbaldehyde in ether at -40°C .⁴¹³



Corey *et al.*⁴¹⁵ have shown that the dehydrochlorination of the α -methoxyalkylphosphonium salts proceeds smoothly under the action of lithium diisopropylamide. The ylides thus obtained have been used for the synthesis of the 9,11-aza-analogues of prostaglandin endoperoxide PGH2 **184**.

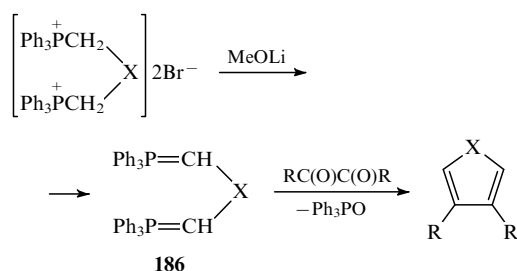


The Wittig-type reactions of triphenylphosphonium alkoxy-methylides with chlorodifluoromethane present a synthetic route to the *gem*-difluoroolefins **185**.⁴¹⁴



$\text{R} = \text{Me}, \text{Bu}^i$.

Bis(triphenylphosphoniomethyl)oxide and -sulfide are converted under the action of lithium methoxide into bis-ylides. The latter are introduced into the Wittig reaction with dialdehydes or diketones for the synthesis of various heterocycles including macrocycles.⁴¹⁶ For instance, the reaction of the ylides **186** with β -diketones gives furan and thiophene derivatives,



$\text{X} = \text{O}, \text{S}$,

with cycloheptatriene-1,6-dicarbaldehyde and biphenyl-2,2'-dialdehyde 4,9-methanooxa[22]-annulenes⁴¹⁷ or nine-membered rings are formed, respectively.^{418, 419} [13]-Annulenes with conjugated double and triple bonds have also been synthesised.⁴²⁰

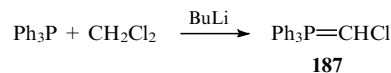
3. C-Halogen-substituted phosphorus ylides

The interest in the C-halogen-substituted phosphorus ylides is caused by the possibility of their application for the preparation of haloalkenes, which are valuable reagents for synthesis.⁴²¹

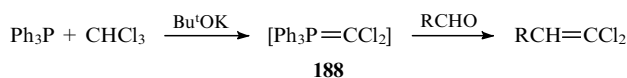
The C-halogen-substituted phosphorus ylides are usually formed in the reaction of tertiary phosphines with any source of mono- or di-halomethylene species.

One of the most common methods for the synthesis of the phosphorus ylides with one or two halogen atoms at the α -carbon

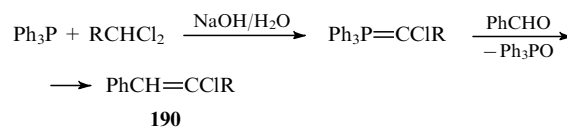
atom involves the addition of the halocarbenes and carbenoids to tertiary phosphines. They are most often prepared by the treatment of polyhalogenmethanes with strong bases in the presence of tertiary phosphine.^{422–427} This method has been used by Seyferth *et al.*⁴²⁵, and Wittig and Schlosser⁴²⁶ for the preparation of triphenylphosphonium chloromethylide **187** from dichloromethane, butyllithium, and triphenylphosphine.



Dichlorocarbene generated from chloroform under the action of potassium *tert*-butoxide reacts with triphenylphosphine to give a suspension of triphenylphosphonium dichloromethylide **188** which is used in the Wittig reaction without isolation from the reaction mixture. The ylide $\text{Ph}_3\text{P}=\text{CCl}$ (**189**) containing chlorine and fluorine atoms at the α -carbon atom has been prepared in the same way.⁴²²

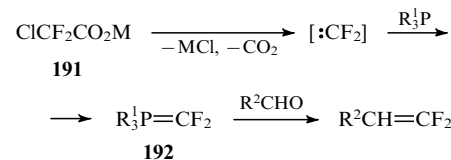


Triphenylphosphonium dichloromethylide **188** has been also synthesised in a heterogeneous medium, dichlorocarbene being generated from chloroform under the action of 50% alkali in the presence of the phase transfer catalyst (TEBA) and triphenylphosphine. In this case ylide in the nascent state enters the Wittig reaction.⁴²⁸ When a benzene solution of chloroform (or dichloromethylthioether), triphenylphosphine, benzaldehyde and a catalytic amount of TEBA was vigorously stirred at room temperature for 1.5 h with 40% aqueous sodium hydroxide, β -chlorostyrenes **190** were prepared in yields of about 40%–50%. This reaction has been used for the preparation of pyrethroids.^{429, 430}

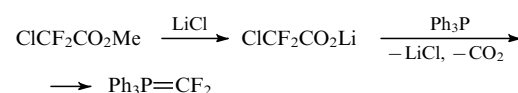


$\text{R} = \text{Cl}, \text{R}'\text{S}$.

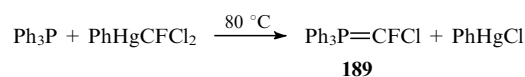
The decarboxylation of the trihalogenacetic acid salts **191** is accompanied by the formation of dihalocarbenes, which, in the presence of tertiary phosphines, give phosphorus ylides **192**; the latter enter into the Wittig reaction with carbonyl compounds.^{431–435} An improvement of this method involves the reaction of triphenylphosphine with methyl chlorodifluoroacetate in the presence of lithium chloride, which presumably proceeds *via* the formation of difluorocarbene.^{436–439}



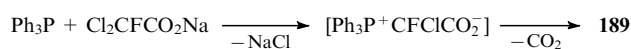
$\text{M} = \text{Li}, \text{Na}, \text{K}, \text{SnMe}_3, \text{R}^2 = \text{Bu}, \text{Ph}$;



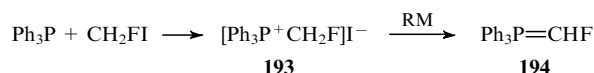
Heating of triphenylphosphine with dichlorofluoromethyl(phenyl)mercury, which is the source of chlorofluorocarbene, yields triphenylphosphonium chlorofluoromethylide **189**.⁴⁴⁰



In some cases the reaction occurs without the formation of dihalocarbene. For instance, sodium dichlorofluoroacetate in a reaction with a tertiary phosphine gives a betaine, which is converted on decarboxylation into triphenylphosphonium chlorofluoromethylide **189**.^{424, 425, 432}

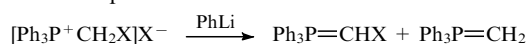


The C-halogen-substituted phosphorus ylides **194** have been obtained by the dehydrohalogenation of halomethyltriphenylphosphonium salts **193** by butyl- and phenyllithium, lithium diisopropylamide, and potassium *tert*-butoxide.^{399, 441–452}

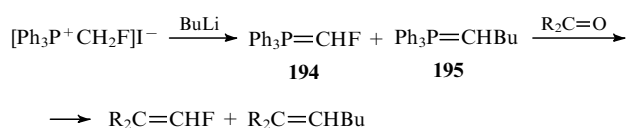


R = Bu, Ph, PrⁱN, Bu^t; M = Li, K.

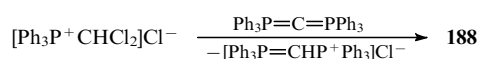
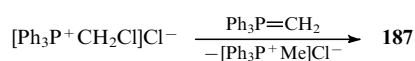
Butyl- and phenyllithium not only deprotonate the phosphonium salt, but can also exchange the halogen atoms at the α-carbon for lithium^{441–452} or a butyl group¹⁴² giving rise to a mixture of ylides **194** and **195**. A mixture of alkenes was formed in the subsequent reaction with carbonyl compounds. The ability of the triphenylphosphonium halomethylides to react with organolithium compounds increases in the series Cl < Br < I.^{449–452}



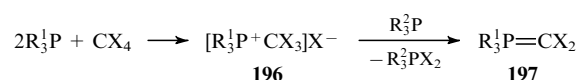
X = Br, Cl, I;



The substitution of butyl- or phenyllithium by a sterically hindered sodium bis(trimethylsilyl)amide allows one to eliminate the side processes.^{443, 444} The dehydrohalogenation of chloromethyltriphenylphosphonium chloride by the unstabilised phosphorus ylides, *e.g.* triphenylphosphonium methylide, occurs very smoothly without side processes and gives a pure triphenylphosphonium chloromethylide **187** in the form of orange crystals with high yields.⁴⁴³ The dehydrochlorination of dichloromethyltriphenylphosphonium chloride by hexaphenylcarbodiphosphorane in aprotic solvents gave dichloromethylide **188** exclusively.^{443, 445}

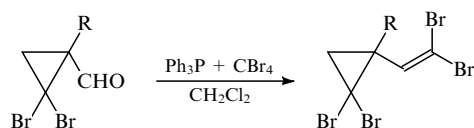


The dehydrohalogenation of trihalomethylphosphonium salts **196**,^{446, 453–467} which are obtained by the reaction of tertiary phosphines with tetrahalomethanes, is an important route for the synthesis of C-halogen-substituted phosphorus ylides.^{449–451, 453} The polyhalomethylphosphonium salts are dehalogenated by tertiary phosphines such as triphenylphosphine or tris(dimethylamino)phosphine.^{458–461}

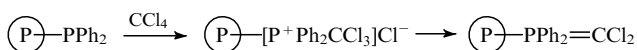


CX₄ = CCl₄, CBr₄, CBr₂Cl₂, CCl₂F₂, CBrCl₃; R² = Ph, Me₂N.

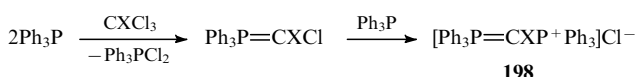
This method has been successfully used in the synthesis of some natural and biologically active compounds, *e.g.* for the preparation of dibromovinyl dibromocyclopropanes.^{446, 461}



This method has also been used for the preparation of the phosphonium dichloromethylides immobilised on a polymer carrier.⁴⁶⁸

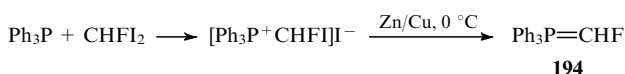
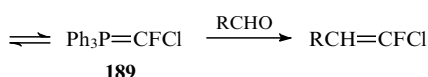
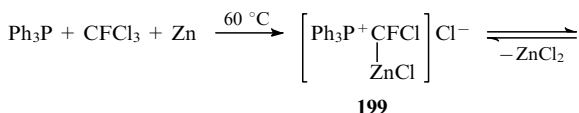


The reaction of triphenylphosphine with tetrahalomethanes may be accompanied by the formation of ylide-phosphonium salts **198** (X = Cl, F), which are used for preparation of halo ketones.^{462–465}

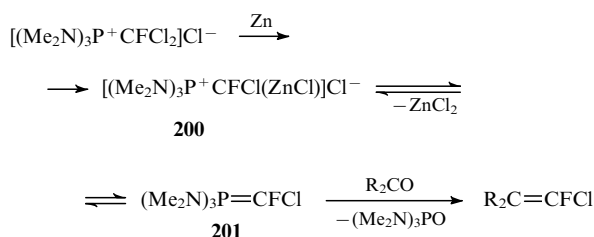


X = Cl, F.

Burton and Van Hamme have proposed to perform dehalogenation of polyhalomethylphosphonium salts by the Group II metals (zinc, cadmium, or mercury).⁴⁵⁶ This procedure gives an organometallic phosphonium salt, which dissociated to a metal chloride and the phosphorus ylide **189**; the latter readily enters into the Wittig reaction with aldehydes and ketones.⁴⁵¹ Heating of triphenylphosphine with chlorotrifluoromethane in the presence of zinc results in the formation of quasi-complex organometallic compounds, which were isolated in the individual form. Analogously, triphenylphosphine reacts with fluorodiodomethane to give a stable fluoroiodomethyltriphenylphosphonium iodide, which is converted into triphenylphosphonium fluoromethylide **194** under the action of a zinc-copper couple.^{142, 447}

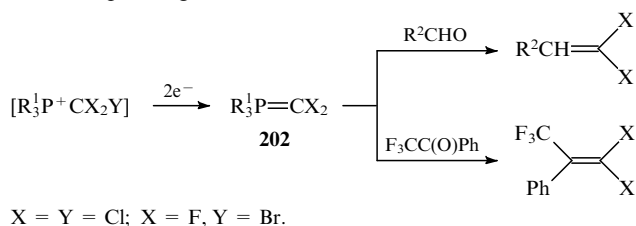


NMR Studies have demonstrated that the reaction of a trihalomethylphosphonium salt with zinc gives the organozinc complex **200**, which dissociates to ZnCl₂ and the phosphorus ylide **201**.³⁸³ The equilibrium is strongly shifted towards the complex **200**. Nevertheless, the Wittig reaction occurs in the presence of a carbonyl compound, which is evidence for the formation of the ylide **201**.^{414, 446}

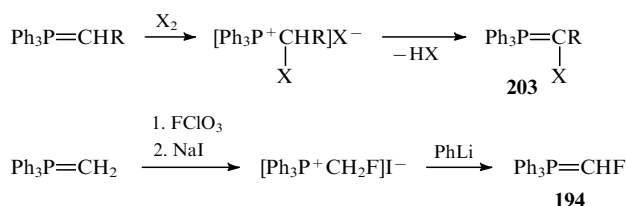


Collignon *et al.* have applied an electrochemical technique for the synthesis of C-halogen-substituted phosphorus ylides. The two-electron electrochemical reduction of dihalo- and trihalomethylphosphonium salts in acetonitrile led to the phosphorus ylides **202**, which enter into the Wittig reaction with aldehydes and

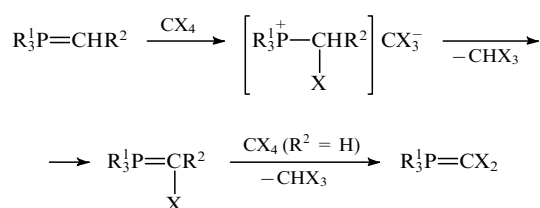
reactive ketones in aprotic medium (DMF or acetonitrile) to yield the corresponding haloalkenes.⁴⁶³



The C-halogen-substituted phosphorus ylides **203** have been synthesised by the halogenation of the phosphorus ylides with hydrogen atoms at the ylide carbon atom. In the case of ylides containing strong electron acceptors at the α -carbon atom (R = CO₂Alk, C(O)Alk, C(O)Ar), the dehydrochlorination of the intermediate phosphonium salt is performed in the presence of triethylamine.⁴⁶⁷ Chlorine, bromine,⁴⁶⁷ phenyliododichloride,⁴⁶⁸ and chloramine T^{469, 470} have been used as halogenating agents. The unstabilised phosphorus ylides are halogenated by perhalo-fluoroalkanes. The reaction occurs regioselectively and high yields of α -haloalkylphosphonium salts are achieved.⁴⁷¹ The fluorination of triphenylphosphonium methylide by FClO₃ followed by NaI gives the fluoromethylphosphonium salt. On its dehydroiodination, triphenylphosphonium fluoromethylide **194** has been obtained in high yield, it enters into the Wittig reaction with aldehydes to form vinylfluorides.⁴⁷²

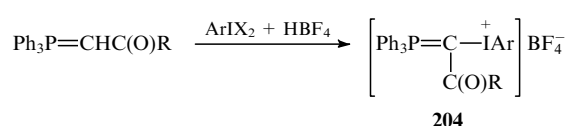


The exchange of a hydrogen atom at the ylide carbon atom for chlorine or bromine occurs on the interaction of phosphorus ylides with carbon tetrachloride and carbon tetrabromide.^{473, 474}



X = Br, Cl.

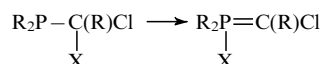
The phosphonium-iodonium ylides **204** have been prepared by the reaction of the stabilised phosphorus ylides with derivatives of trivalent iodine.⁴⁷⁵



X = F, OAc, X₂ = O; Ar = Ph, 2-MeC₆H₄;

R = EtO, Ph, 4-MeC₆H₄.

The halogen atom at the α -carbon atom of the tertiary alkylphosphines is highly mobile, which determines its migration towards the phosphorus atom, the 1,2(C $\rightarrow$ P)-halogenotropic shift.

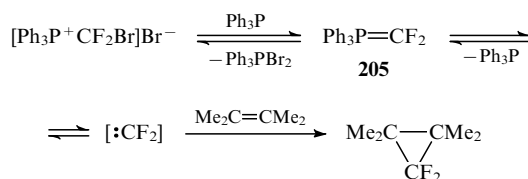


α -Haloalkylphosphines containing electron-accepting substituents at the α -carbon atom rearrange rather easily into phosphorus ylides, and the halogen atom in such ylides may be substituted by various substituents. Numerous examples of the preparation of phosphorus ylides by this method have been described.^{12, 476–483}

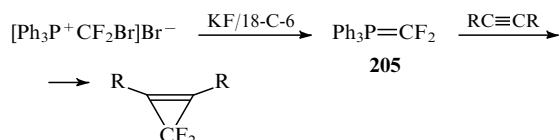
The C-halosubstituted phosphorus ylides have been studied in detail using quantum-chemical calculations and physicochemical methods. The *ab initio* quantum-chemical calculations performed by Dixon⁴⁸⁴ and Bestmann¹⁶ have shown that the C-fluorine-containing ylide H₃P=CHF has a non-planar P=CHF group with an inversion barrier of about 2.8 kcal mol⁻¹. Francl *et al.*⁴⁸⁵ have assumed, in accordance with Dixon's results, that the zwitter-ionic character of the P=C bond in the H₃P=CF₂ molecule is minimal. On the basis of the differences in electron densities it has been concluded that the introduction of a fluorine atom at the α -atom enhances the π -character of the P=C bond.

The alkoxy-carbonyl- and acylfluoromethylides exist as mixtures of two geometrical isomers. This is a result of hindered rotation about the P=C bond, caused by partial enolisation of the compounds with considerable shift of the negative charge to the carbonyl oxygen atom.⁴⁴¹

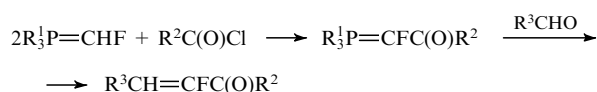
The stability of the C-halogen-containing phosphorus ylides depends on the electron-accepting properties of the second substituent at the ylide carbon atom. The C-halogenoylides stabilised by strong electron-accepting substituents can be isolated and purified, while non-stabilised ylides with one or two halogen atoms at the α -carbon atom are unstable and thus they are usually introduced in subsequent reactions without isolation and purification.^{443, 445} Only triphenylphosphonium chloromethylide⁴⁴³ and -dichloromethylide⁴⁴⁶ have been isolated in pure state. Triphenylphosphonium difluoromethylide **205**, which has been prepared by the reaction of bromodifluoromethyltriphenylphosphonium bromide with tertiary phosphines or with potassium fluoride in the presence of 18-crown-6 dissociates readily into difluorocarbene and triphenylphosphine. Difluorocarbene has been captured by tetramethylethylene. The formation of 1,1-difluoro-2,2,3,3-tetramethylcyclopropane in solution indicated the presence of difluorocarbene.⁴⁸⁶



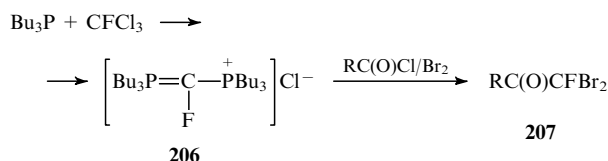
Schlosser *et al.*⁴⁸⁷ have recently demonstrated that difluoromethylide **205** adds to mono- and disubstituted acetylenes to give difluorocyclopropenes in good yield.



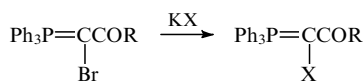
The alkylation, acylation, and arylation of simple fluoromethylides leads directly to C-substituted fluoromethylides as a result of transylidation and presents a convenient synthetic route to various fluoroalkenes.⁴⁶⁷



The acylation of C-fluoro-substituted ylides **206** obtained by the reaction of tributylphosphine with trichlorofluoromethane followed by bromination is a convenient way for the preparation of haloalkyl ketones.⁴⁶⁵

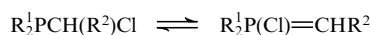


The reactions of C-bromo-substituted ylides with potassium iodide or thiocyanate result in the substitution of the bromine atom at the ylide carbon atom by iodine or a thiocyanato group.^{467, 489}



X = I, SCN.

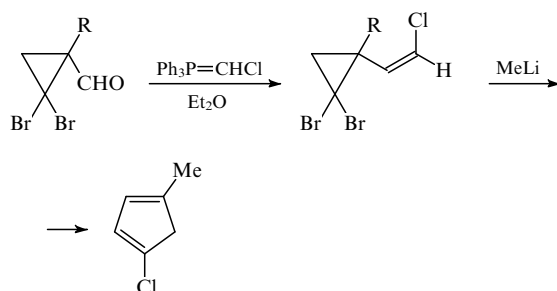
The α -haloalkylphosphines exist in a tautomeric equilibrium with ylides containing the halogen at the phosphorus atom, therefore, they manifest the chemical properties characteristic of both trivalent phosphorus and ylides. The ratio of the tautomers depends on the electron-accepting properties of the substituents at the α -carbon atom: electron-accepting substituents shift the equilibrium towards the ylides, while electron-donating substituents, on the contrary, increase the equilibrium concentration of α -haloalkylphosphines.^{489–492}



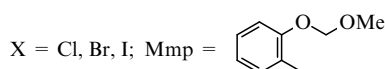
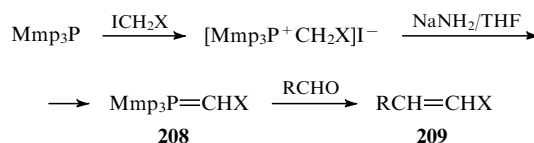
R² = Cl, Br, Alk, Ar.

The C-halogen-substituted phosphorus ylides are valuable reagents in the synthesis of haloalkenes. Electron-accepting halogen atoms at the ylide carbon atom decrease the nucleophilicity of the phosphorus ylides. Therefore, triphenylphosphonium haloalkenylides readily alkenate aldehydes and activated ketones, and do not alkenate non-activated ketones and carboxylic esters. The reactivity of haloalkenylides may be enhanced by introducing electron-donating substituents at the phosphorus atom, e.g., dimethylamino groups, which decrease the electrophilicity of the phosphonium group. Tris(dialkylamino)phosphonium ylides demonstrate definite advantages as haloalkenating reagents over the triphenylphosphonium ylides. For instance, tris(dimethylamino)phosphonium dichloromethylide converts ethyl-*cis-trans*-cinnamaldehyde into chrysanthemic acid in high yield, which could not be achieved with triphenylphosphonium ylide **187**.^{453, 457–459}

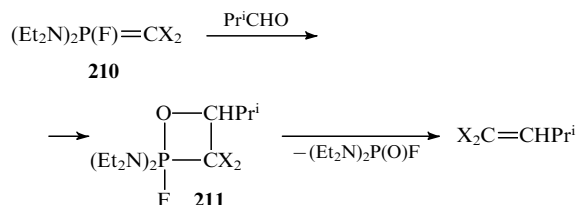
The haloalkenylsubstituted dibromocyclopropanes, the initial compounds for the synthesis of cyclopentadienes, and alkenes, have been obtained using triphenylphosphonium chloromethylide.⁴⁶¹



Schlosser has proposed a highly stereoselective method for the synthesis of haloalkenes, which involves 2-methoxymethoxyphenylphosphonium ylides **208** instead of triphenylphosphonium ylides. In this case, the ratio of *cis-trans* isomers of alkenes **209** was 98 : 2–99 : 1.⁴²⁷

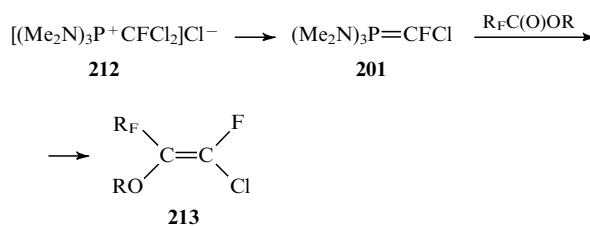


The reaction of aldehydes with the ylide **210** containing a fluorine atom at the phosphorus atom yielded the four-membered cycloadducts of the Wittig reaction, **211**, which have been isolated in the individual form; their structure was studied by NMR. On heating to 60–80 °C, the adducts decomposed into 1,1-dihaloalkenes and bis(diethylamino)phosphoryl fluoride.⁴⁹³



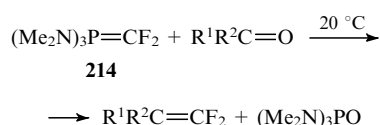
X = Cl, Br.

The interaction of tris(dimethylamino)phosphonium chlorofluoromethylide **201** with fluoroalkylcarboxylic esters is stereoselective and occurs with the predominant formation of *Z*-isomers of alkyl polyfluoroalkenyl ethers **213**.



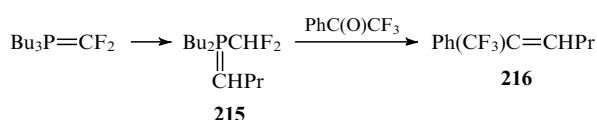
However, monofluoro-, fluorochloro-, and bromofluoromethylides usually react with aldehydes and asymmetrical ketones to give mixtures of *Z*- and *E*-alkenes.^{383, 384} The yields and the stereochemistry of the Wittig reaction in the case of tris(dimethylamino)phosphonium haloalkenylides depend on the method of dechlorination of the phosphonium salt. A high yield of (*Z*)-1-chloro-2-propoxyperfluoropropene is achieved in the case of dechlorination of the salt **212** with tris(dimethylamino)phosphine in the presence of isopropyl trifluoroacetate.^{446, 453–456} The zinc–copper couple dehalogenates exothermally the phosphonium salts **212** in the presence of carbonyl compounds R¹R²C=O (R¹ = Ph, C₆H₁₃, CF₃; R² = H, Ph, CF₃, Me, AlkO), with the formation of 1-chloro-1-fluoroalkenes. In the case of aldehydes and activated ketones, the yields of alkenes are almost quantitative, while with ketones of the acetophenone type the yields are about 70%.

The difluoromethylide **214**, which is generated from tris(dimethylamino)phosphine and dibromofluoromethane, is a convenient source of the difluoromethylene group; **214** enters into the Wittig reaction with cyclohexanone, acetophenone, and propiophenone.^{453, 455, 456}

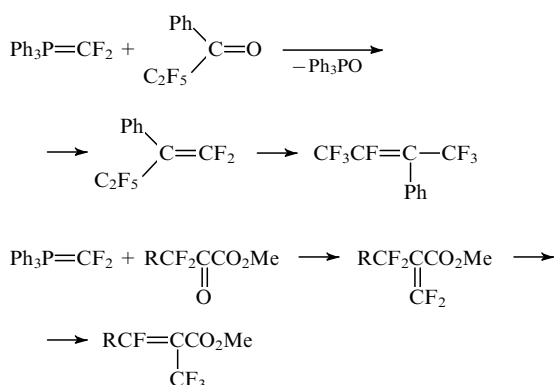


Triphenylphosphonium fluoromethylide **194** alkenates aliphatic and aromatic aldehydes, and activated and non-activated ketones.^{142, 448} Triphenylphosphonium fluorochloromethylide **189** generated in the reaction of triphenylphosphine with sodium

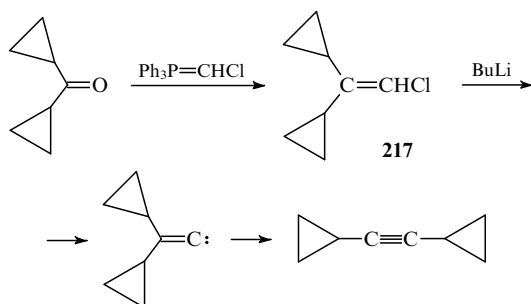
dichlorofluoroacetate acid enters into the Wittig reaction with aldehydes and activated ketones to yield 1 : 1 mixtures of *Z*- and *E*-alkenes in 1 : 1 ratio,^{142, 448} and alkenates aromatic α -oxocarboxylic esters with formation of α -aryl chlorofluoroacrylic acids.^{423, 424, 436, 437, 494–496} Triphenylphosphonium difluoromethylide **205** converts aldehydes and activated ketones into α, α -difluoroolefins in high yields; however, it does not alkenate cyclohexanone and acetophenone because of their insufficient electrophilicity. Tributylphosphonium difluoromethylide has high reactivity owing to the electron-donating effect of the butyl groups. This ylide, generated by the haloacetate method, alkenates *in situ* such non-activated ketones as benzophenone, cyclohexanone, methylketones $\text{RC}(\text{O})\text{Me}$, where $\text{R} = \text{C}_5\text{H}_{11}$, Ph, 2-furyl, 2-thienyl, *etc.*^{436, 437} Examples of anomaly in the course of the Wittig reaction with tributylphosphonium difluoromethylide are known. For instance, in the reaction of tributylphosphonium difluoromethylide with trifluoroacetophenone, a prototropic rearrangement of the difluoromethylide into the butylide **215** yields the alkene **216**.^{431, 436}



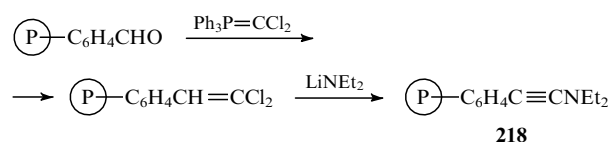
The Wittig reaction of *C*-fluoro-substituted ylides with ketones containing perfluoroalkyl groups is sometimes accompanied by isomerisation associated with the migration of the fluorine atom from the perfluoroalkyl to difluoromethylene group.⁴³² The isomerisation of fluoroalkenes is suppressed when the reaction is performed in the absence of strong bases or dehalogenating agents.⁴³¹



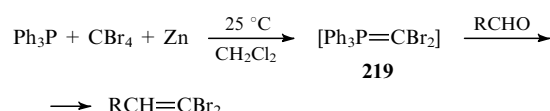
The reaction of triphenylphosphonium chloromethylide with dicyclopentyl ketone gives the chloroalkene **217** in 81% yield; it is transformed into dicyclopentylacetylene, which is formed *via* a carbenoid.⁴⁹⁷



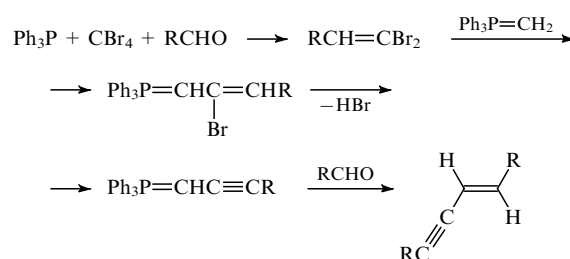
Triphenylphosphonium dichloromethylide was used for the modification of polymeric reagents, for instance, for the preparation of polymeric ynamines **218**.⁴⁹⁸



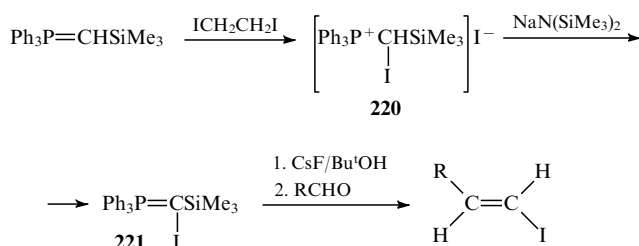
Corey has proposed a convenient method for the synthesis of haloalkenes by the reaction of triphenylphosphine with carbon tetrabromide in the presence of zinc dust.⁴⁹⁷ The dibromomethylide **219** reacts *in situ* with aldehydes to form dibromoalkenes⁴⁹⁴ that have been used in the synthesis of retinoids,⁴⁹⁴ alkynes,⁴⁹⁷ and alkynecarboxylic acids.^{359, 446}



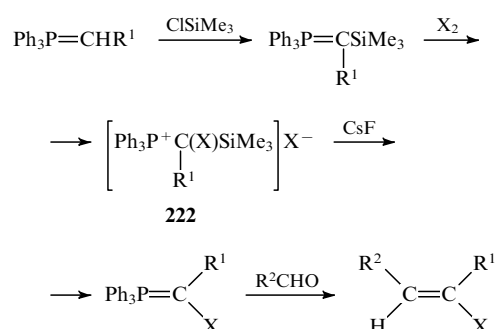
Bestmann has prepared synthons of pheromones based on the *C*-halogen-substituted ylides.⁴⁹⁹



Methods for the preparation of α -haloalkenes on the basis of *C*-silicon-substituted ylides have been developed. The mild iodination of triphenylphosphonium trimethylsilylmethylide with 1,2-diiodoethane gives the iodoalkylphosphonium salt **220** in high yield. The dehydroiodination of the salt **220** by sodium bis(trimethylsilyl)amide results in the formation of the trimethylsilyliodo-methylide **221**, which is stereoselectively transformed into α -iodoalkenes on treatment with cesium fluoride in *tert*-butyl alcohol in the presence of carbonyl compounds.⁵⁰⁰

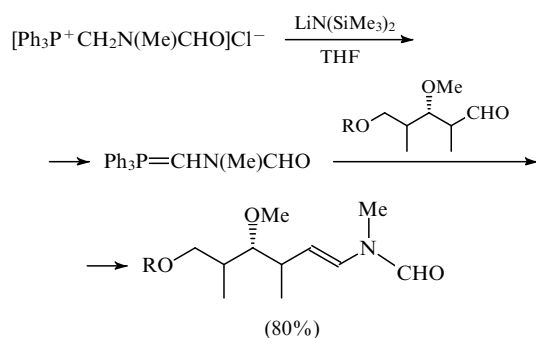


The successive treatment of non-stabilised phosphorus ylides by chlorotrimethylsilane and halogen yields α -haloalkyl α -trimethylsilyl-triphenylphosphonium salts **222**, their desilylation by cesium fluoride in the presence of aldehydes results in haloalkenes.⁵⁰¹

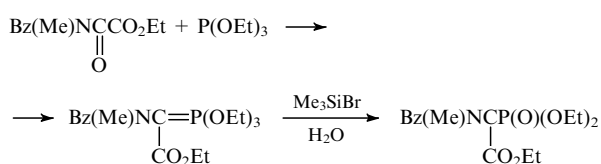


V. Conclusion

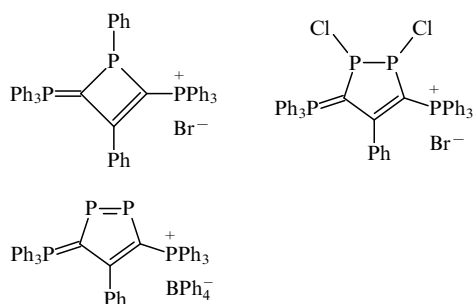
Heteroatoms at the ylide carbon atom thus considerably affect the chemical properties and the reactivity of the phosphorus ylides. Certain heteroatoms, such as the atoms of the main Group I and II, nitrogen, tin, and lead atoms increase the electron density at the carbon atom and the reactivity of ylides, while on the contrary, other heteroatoms such as silicon and germanium atoms, Group V–VII atoms and transition elements stabilise the ylide carbanion, thus lowering its nucleophilicity. As a result, C-substituted phosphorus ylides acquire new remarkable chemical properties and offer new synthetic opportunities. This determines the deep interest of chemists in the C-hetero-substituted phosphorus ylides as exceptionally promising reagents in organic synthesis.⁵⁰² Thus after the present review has been completed, new data on the chemistry of the C-element-substituted phosphorus ylides, especially ylides containing Group V main elements at the α -carbon atom appeared. Paterson *et al.*⁵⁰³ have synthesised N-methylformamido-substituted phosphorus ylide by the action of lithium bis(trimethylsilyl)amide on the phosphonium salt. This ylide was shown to be an effective reagent for the transformation of aldehydes into the corresponding N-alkenyl-N-methylformamides.



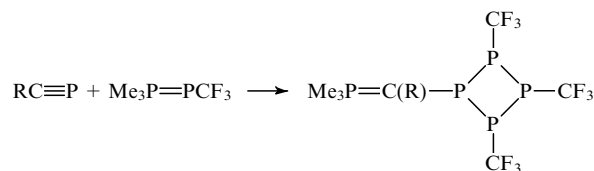
Japanese chemists have synthesised trialkoxyphosphonium ylides with a nitrogen atom at the ylide carbon atom and converted them into the α -alkylaminophosphonates.⁵⁰⁴



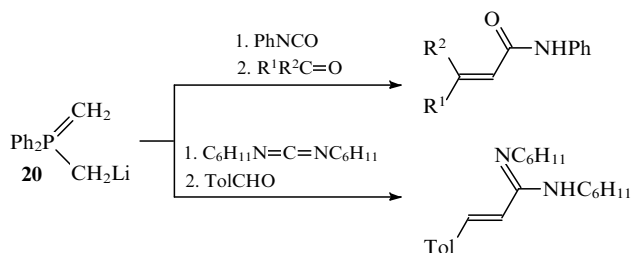
C-Phosphino-substituted phosphorus ylides have been also intensely studied. Schmidpeter *et al.*⁵⁰⁵ have synthesised four- and five-membered heterocycles with an exocyclic ylide group including heterocycles with a double P=P bond.



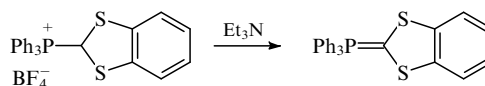
Grobe⁵⁰⁶ has performed a very interesting synthesis of a phosphorus ylide with a tetraphosphetene ring at the α -carbon atom starting from the derivatives of mono- or two-coordinate phosphorus.



Cristau *et al.*⁵⁰⁷ have studied the reactivity of ylide-anions **20** towards carbodiimides and isocyanates. The reaction is performed in two steps: at first heterocumulene is treated with the ylide-anion, and then the ylide adduct is introduced in the reaction with an aldehyde or ketone. As a result, α,β -unsaturated amides and amidines are formed in high yields and stereoselectivity.



Clausen and Becher⁵⁰⁸ have described a new synthetic route to tetrathiafulvenes from cyclic dithiosubstituted phosphorus ylides, which were generated from the corresponding phosphonium salts by the action of triethylamine.



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Chemical problems of the infrared sensitisation of photographic materials

B I Shapiro

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Abstract. The mechanisms of the spectral sensitisation of silver halides by infrachromatic dyes are examined. It is concluded that the effectiveness of the spectral sensitisation is determined by secondary dark oxidation reactions of the silver atoms formed — the so called dye self-desensitisation processes in which the infrachromatic dye plays the role of a catalyst — rather than by primary steps involving electron transfer from the photoexcited dye to AgHal. It is shown that processes involving the super sensitisation of infrared photographic materials constitute the inhibition of the dye self-desensitisation reactions. Supersensitisers are classified in terms of their inhibition mechanism as supersensitisers of the first and second kind. The application of supersensitisers of the first and second kind leads to a super-additive increase in light sensitivity. The modern supersensitisation methods have made it possible to develop a new generation of infrared films with improved photographic parameters. For example, the photosensitivity of an infrared film with a sensitisation maximum at 1060 nm has been increased by a factor of 100. The possibility of spectral sensitisation up to 1500 nm is demonstrated. The bibliography includes 147 references.

I. Introduction

The spectral sensitisation of silver halide (AgHal) photographic materials is one of the few examples of a highly effective spectral sensitisation process devised by man. The discovery of the spectral sensitisation of silver halides by organic dyes (Dy) is one of the most important events in the history of photography. It was achieved in 1873 by Prof. Herman Wilhelm Vogel.¹ In the course of the 120 years history of its development, the spectral sensitisation process was raised to an extremely high level of perfection. It is sufficient to state that the relative quantum yield of the spectral sensitisation in the visible region of the spectrum is close to unity, *i.e.* the photographic effectiveness of the quanta absorbed by the dye is equal to the effectiveness of the quanta absorbed by the AgHal lattice.

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The expansion of the region of spectral sensitivity into the infrared emission zone is known to encounter considerable, seemingly insurmountable, difficulties. In the first place, an appreciable decrease in the sensitisation with increase in the emission wavelength is observed.² Until recently there was an empirical rule, according to which light sensitivity diminishes on moving into the IR region of the spectrum approximately by an order of magnitude for each 100 nm. A particularly marked decrease in light sensitivity occurs in the region of the spectrum at wavelengths exceeding 1000 nm. The sensitivity of a photographic material with a sensitisation maximum in the region of 1000 nm is approximately 1000 times smaller than the sensitivity of the light-sensitive layers in the visible region of the spectrum. The spectral sensitivity limit corresponds to the range 1300–1350 nm.^{3,4}

Yet another difficulty is the insufficient viability of infrachromatic photographic materials. An appreciable decrease in light sensitivity and an increase in the fogging of the light-sensitive layers is observed in the course of time, which makes them unsuitable for use a short time after their preparation. The question of the causes of the decrease in the effectiveness of their spectral sensitisation in the IR region of the spectrum has been widely discussed in the literature (see, for example, Refs 2, 5, and 6). In the dominant concept, the decrease in the light sensitivity of infrared light-sensitive layers is attributed to the energy 'deficit'. According to this concept, a light quantum absorbed by an infrared dye is significantly smaller than the quantum absorbed by AgHal and for this reason it cannot exert the same photochemical effect. Nevertheless, there are numerous experimental facts indicating the important role of secondary chemical reactions with participation of the spectral sensitiser, which determine to a large extent the effectiveness of the spectral sensitisation process.^{5,6} The aim of the present review is to compare various experimental results and to analyse the theoretical approaches to the problem of infrared sensitisation.

II. The problem of the energy 'deficit'

The main problem which arises in the spectral sensitisation of wide-band semiconductors (silver halides) by organic dyes is that of the energy 'deficit'. The theory of spectral sensitisation is invoked primarily in order to explain how a lower-energy photon, absorbed by the spectral sensitiser, exerts the same photographic effect as the higher-energy quantum absorbed by the AgHal lattice. For example, the width of the forbidden band of AgBr is

2.6 eV (~ 500 nm absorption limit). However, the spectral sensitisation by dyes is observed in the IR region of the spectrum in the vicinity of 750–1100 nm, *i.e.* the sensitisation takes place under the influence of light quanta with a significantly smaller energy (1.6–1.1 eV).

It is noteworthy that the problem of energy 'deficit' can be readily solved within the framework of the theory of the resonance transfer of excitation energy from the dye to AgHal when the local electronic levels of the photoconductor participate in the photo-process. Excitation energy transfer in spectral sensitisation was first examined in 1948 by Mott,⁷ who put forward the hypothesis that, in the sensitised photolysis of AgBr, the light energy absorbed by the dye is consumed in the liberation of an electron at a local level in the forbidden band. This scheme was developed in detail in the 1960s in the studies of Terenin, Akimov, and coworkers^{8–11} and of Kuhn, Möbius, and coworkers.¹² The possibility of spectral sensitisation *via* the excitation energy resonance transfer mechanism has been demonstrated experimentally by Akimov¹¹ and Kuhn and coworkers.¹² However, it was later concluded¹³ that the spectral sensitisation of real AgHal emulsions is determined by electron transfer from the photo-excited dye (Dy^*) to AgHal and that the contribution of the excitation energy resonance transfer does not exceed several per cent. At the present time, the electron transfer mechanism has become generally accepted.²

The electron transfer mechanism in the spectral sensitisation of AgHal by dyes was first examined by Gurney and Mott¹⁴ within the framework of the band model of silver halides in 1938. According to this mechanism, the spectral sensitisation is associated with electron transfer from the photoexcited dye Dy^* to the conduction band (CB) of silver halide. According to Gurney and Mott,¹⁴ for effective sensitisation the energy level of the photo-excited electron in Dy^* must be above the bottom of the conduction band of AgHal or at least close to it. In subsequent steps, the recombination of the electrons injected into the conduction band with the interstitial (or surface) Ag^+ ions, which takes place preferentially on the sensitivity centres (SC), results in the formation of a latent photographic image. The dye can return from the radical-cation ($\text{Dy}^{+\cdot}$) state to the initial state either *via* the injection of a hole into the valence band (VB) of silver halide or by the acceptance of an electron from defective surface sites, for example, from defective Br^- and I^- ions or the impurity centres (IC) formed during chemical sensitisation.

The determination of the positions of the electronic levels of the dyes adsorbed on AgHal in terms of the absolute potential scale is a fairly complex task. There exist both experimental methods for such determination and computational quantum-chemical methods. The lowest vacant level of the dye ϵ_{lv} , to which an electron is transferred on photoexcitation, may be characterised by the electron affinity of the dye E_{ads} . The highest occupied level ϵ_{ho} , from which an electron passes to ϵ_{lv} on photoexcitation is in its turn determined by the ionisation potential of the dye I_{ads} . Numerous attempts have been made to determine E_{ads} and I_{ads} (see James's monograph² and the communications quoted therein), but, owing to the difficulties arising in the interpretation of the experimental results, it is at present impossible to determine unambiguously the levels ϵ_{lv} and ϵ_{ho} of adsorbed dyes.

The energy levels of the dyes can be calculated by different quantum-chemical methods. The first systematic studies on these lines were carried out by Tani and Kikuchi.¹⁵ Electrochemical potentials and in the first place the polarographic half-wave reduction ($E_{1/2}^{\text{Red}}$) and oxidation ($E_{1/2}^{\text{Ox}}$) potentials of dyes have found extensive application in studies on spectral sensitisation for the determination of the energy levels of the dyes.^{2, 15–17} The potential $E_{1/2}^{\text{Red}}$ reflects the energy of the level ϵ_{lv} of Dy^* from which an electron is transferred to the conduction band of AgHal while $E_{1/2}^{\text{Ox}}$ reflects the energy of ϵ_{ho} .

The polarographic half-wave reduction and oxidation potentials of dyes are at present the principal energy criteria of the electronic levels in dyes. They are frequently resorted to instead of

the quantities ϵ_{lv} and ϵ_{ho} . The main reason for this is the ease of their determination. A definite relation between the positions of the electronic levels, characterised by the oxidation-reduction potentials of dyes, and the efficiency of the spectral sensitisation has been demonstrated in numerous studies. Mention should be made in the first place of the studies of Dähne,^{18, 19} Tani and Kikuchi,¹⁵ Gilman,¹⁶ and a number of other investigators (see the relevant reviews^{19–23}). A definite relation between the positions of the electronic levels of dyes, characterised by the potentials, and the efficiency of the spectral sensitisation was discovered in these studies. For example, it has been shown that, as the location of ϵ_{lv} becomes deeper, *i.e.* in a definite range of potentials $|E_{1/2}^{\text{Red}}|$ (as a rule, $|E_{1/2}^{\text{Red}}| < 1.0$ V relative to the saturated calomel electrode), a decrease in the effectiveness of the spectral sensitisation of negative photographic materials is observed. This is associated with the fact that, starting with a certain boundary value of $E_{1/2}^{\text{Red}}$ (Dy), the levels ϵ_{lv} are found to be deeper than the bottom of the conduction band of AgHal, which hinders the transfer of a photoelectron from Dy^* to the conduction band. The positions of the bottom of the conduction band and of the top of the valence band of AgBr have been determined⁵ in terms of the electrochemical potential scale. Relative to the normal hydrogen electrode (n.h.e.), the potential of the bottom of the conduction band of AgBr is -1.1 V, while the potential of the top of its valence band is $+1.5$ V. Relative to the saturated calomel electrode (sat. c.e.), these potentials are -1.34 and $+1.26$ V respectively. The potential of the bottom of the conduction band is close to the boundary value $E_R^* = -1.37$ V established later in a study by Tani.²⁴

The bathochromic shift of the absorption by cyanine dyes to the IR region of the spectrum is known to be attained as a rule when the length of the polymethine chain is increased. With increase in the length of the polymethine chain, the levels ϵ_{lv} become deeper and approach the levels ϵ_{ho} .¹⁵ Fig. 1 illustrates the energy level diagram for thiapolymethine dyes in terms of the electrochemical potential scale relative to the AgBr bands. The potentials were taken from Shapiro *et al.*²⁵ Starting with the carbocyanine for which $n = 1$, the levels ϵ_{lv} of the dye are found to lie below the bottom of the conduction band of AgBr and are located increasingly deeper with increase in n (*i.e.* as the absorption shifts into the IR region of the spectrum). Seemingly, the problem of the effectiveness of spectral sensitisation, namely the decrease in the effective sensitisation as the level ϵ_{lv} of the dye assumes a deeper position $|E_{1/2}^{\text{Red}}(\text{Dy})| < 1.34$ V relative to the sat. c.e., may be solved successfully within the framework of the energy approach to electron transfer. The energy gap (energy

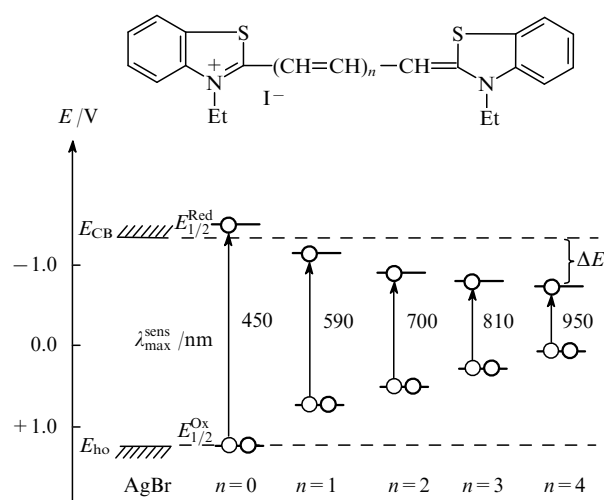


Figure 1. Energy level diagram for thiapolycarbocyanine dyes on the electrochemical potential scale (relative to sat. c.e.).

'deficit') between ε_{IV} and the bottom of the conduction band then increases. In this case, the decrease in spectral sensitivity with increase in the energy gap (ΔE) is quite reasonable, since the sensitisation rate constant k_S which determines the quantum yield of the spectral sensitisation should vary exponentially with ΔE :

$$k_S = A \exp\left(-\alpha \frac{\Delta E}{RT}\right), \quad (1)$$

where A and α are constants. This explanation of the dependence of the spectral sensitivity on $E_{1/2}^{\text{Red}}(\text{Dy})$ can in fact be found as a rule in the literature.

Despite the agreement between the experimental results and the predictions of the theory of electron transfer from Dy^* to the AgHal conduction band noted above, a certain amount of caution must be exercised in assessing the adequacy of this model. The question of the real disposition of the dye levels relative to the AgHal electron energy bands has been discussed hitherto. The mutual assignment of the levels based on photographic experiments, electrochemical data, and quantumchemical calculations, is also not unambiguous. However, the principal disadvantage of the electron transfer model considered is the absence of a dependence of the spectral sensitivity on $E_{1/2}^{\text{Red}}(\text{Dy})$ when the light-sensitive layers are exposed *in vacuo*.

The studies by James and coworkers^{26–28} of the influence of the evacuation of photographic emulsions on the effectiveness of spectral sensitisation are undoubtedly some of the most important in the field of spectral sensitisation. It was shown in these investigations that, after the removal of oxygen and water from light-sensitive layers by evacuation and the additional reductive sensitisation by hydrogen, the dependence of the sensitisation effectiveness on $E_{1/2}^{\text{Red}}(\text{Dy})$ vanishes and many desensitising dyes, the ε_{IV} levels of which are located deep under the conduction band, become effective sensitisers. For example, spectral sensitisation has been observed for a dye with $E_{1/2}^{\text{Red}}(\text{Dy}) = -0.36$ V, for which the transfer of a photoelectron from Dy^* to the AgHal conduction band is virtually impossible ($\Delta E = 1.1$ V). This was a kind of crucial experiment, which demonstrated convincingly that the effectiveness of the spectral sensitisation is determined not so much by the disposition of the dye levels relative to the AgHal bands as by the chemical reactions with participation of oxygen and water protons, which lead to the formation of secondary products (in particular, hydrogen peroxide) and which thereby divert the photoelectrons from the formation of a latent image. A similar influence of evacuation on spectrally sensitised layers has been observed also by other investigators.^{28, 29}

In order to account for the sensitisation by dyes the ε_{IV} levels of which are located under the AgHal conduction band, James employed a two-stage electron transfer from Dy^* to AgHal,³⁰ according to which the electron is initially transferred not to the conduction band but to local surface capture levels located deeper (or near) the electronic level in Dy^* . Such levels may be surface defects and in the first place surface Ag ions (on kink sites). Electrons are next thermally excited from the surface capture levels to the AgHal conduction band. The transfer of electrons from Dy^* to local surface layers, including the silver ion levels, has also been examined by West³¹ and Mitchell.³² Gilman¹⁶ also postulates that the number and depth of the effective electron capture levels on AgHal are more important factors, controlling the sensitising effect of the dye, than the relation between the energy levels of the dye and AgHal. The spectral sensitisation processes 'under the conduction band' with participation of surface electron traps have also been examined by Gilman.³³

James's two-stage mechanism³⁰ was a logical continuation of the conclusions arising from his study³⁴ and also from that of Saunders and West³⁵ concerning the mechanism of the development process. In his earlier study,³⁴ James showed that, for microcrystals with subsurface sensitivity, the deep latent image undergoes latensification when the microcrystals come into contact with a number of developing substances (hydrazine, hydrox-

ylamine, phenidone, *etc.*), capable of effecting the transfer of one electron, while Saunders and West³⁵ observed the formation of a latent image on AgHal single crystals at a depth of several microns under the surface when they come into contact with a normal developer. The single-stage electron transfer from developers into the bulk of AgHal is unrealistic, since, for a width of the energy gap $\Delta E = 1.3$ V between the electronic level in the developers and the bottom of the conduction band, the transfer time should be approximately 100 years.

The electron transfer from the silver atom formed on surface development of AgHal into the exposed crystals constitutes the basis of the generation of a direct negative image when a fogging developer is employed³⁶ and also when light-sensitive layers initially exposed in a surface developer are subjected to uniform illumination by low-intensity light.²

Convincing evidence for electron transfer from Dy^* into the bulk of AgHal *via* the system of levels under the AgHal conduction band is provided by experiments with AgHal emulsions containing Ir^{3+} ions in microcrystals. Gilman³⁷ showed that a deep latent image is formed in such emulsions on spectral sensitisation by dyes with $E_{1/2}^{\text{Red}}(\text{Dy})$ up to -0.25 V (relative to the Ag/AgCl electrode). Thermal excitation of electrons to the conduction band has been considered.

If one takes into account the appreciable oxidation potential of the Ag^+/Ag system, then the surface silver ions can be reduced by virtually any photoexcited infrared dye.²³ It is noteworthy that, even in the presence of the excess of Br^- ions actually employed in the emulsion, the AgHal surface coated by the excess bromide ions constitutes less than 20% of the entire surface,³⁸ *i.e.* silver ions are always present on the surface.

It is well known that the effectiveness of the spectral sensitisation of AgHal by dyes with ε_{IV} levels located under the conduction band, and in the first place by infrachromatic dyes, depends greatly on the concentration of Ag^+ ions (pAg) in the emulsion. The spectral sensitivity S_λ then increases with increase in the Ag^+ concentration.² The dependence of the effectiveness of infrared dyes on pAg has been studied in detail by Collier and Gilman,³⁹ who noted an increase in the effectiveness of spectral sensitisation for dyes having a long polymethine chain with decrease in pAg. The increase in S_λ with increase in the concentration of Ag^+ ions has been attributed to the direct phototransfer of electrons from Dy^* to surface Ag^+ ions. Within the framework of the band scheme of the AgHal levels, this is equivalent to the downward bending of the bands and the approach of the bottom of the conduction band to ε_{IV} of the dye, as shown in Fig. 2. The dependence of the boundary potentials and $E_{1/2}^{\text{Red}}$ and $E_{1/2}^{\text{Ox}}$, corresponding to the injection of the dye electrons and hole into AgHal, on pAg, discovered by Berriman and Gilman,⁴⁰ is associated with this finding. Under these conditions, the injection of electrons from Dy^* into AgHal is facilitated at low pAg, while the injection of holes is facilitated at high pAg.

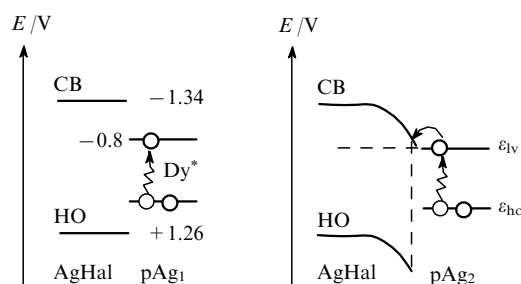


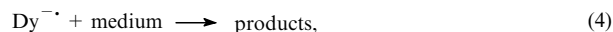
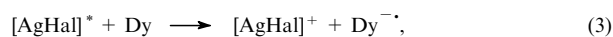
Figure 2. Schematic illustration of the bending of the AgHal bands with increase in the concentration of Ag^+ ions ($\text{pAg}_1 < \text{pAg}_2$) in a photographic emulsion during spectral sensitisation by a dye with a deep ε_{IV} level.

When the spectral sensitisation by infrared dyes is considered as a reaction of Dy^* with surface Ag^+ ions, the main problem becomes not the energy 'deficit' but the effectiveness of the separation of the charges formed in the primary step and hence the probability of the recombination of the charges or their irreversible binding. It is noteworthy that this is the usual problem, characteristic of all chemical oxidation-reduction reactions, which is solved mainly by the stabilisation of the final states. In the case of silver halides, such stabilisation is possible by virtue of the rapid relaxation of the generated states as a result of the electrostatic interaction with the medium and also because of the subsequent removal of electrons through space by their relay migration *via* surface (or subsurface) silver ions or *via* impurity cations. The uniqueness of silver halides in this respect may be determined by the greater probability of the formation of silver molecules (the latent image precentres), whereupon the energy of the interatomic $\text{Ag}-\text{Ag}$ bond is gained.

If it is supposed that the primary step consists in electron transfer to surface traps and in the first place to silver ions, the difference in the photographic effect of infrared dyes is determined not so much by the kinetics of the primary step as by the kinetics of the secondary reactions of the components of the photographic emulsion, involving the formation of silver atoms, and in the first place of the chemical processes involving the oxidation of the silver atoms and silver particles formed. The influence of chemical reactions, including reactions involving oxygen and protons, on the effectiveness of the photographic process is well known.¹⁸ This concerns the so called processes involving the desensitisation of AgHal by dyes.

III. Desensitisation of silver halides by dyes

The desensitisation of AgHal by dyes is understood as the decrease in the intrinsic (blue) sensitivity of the photographic emulsion following the adsorption of dyes on AgHal microcrystals. The desensitisation of AgHal was first examined by Lüppo-Cramer,⁴¹ who introduced the term desensitisation. Two principal desensitisation mechanisms are distinguished — electron acceptor and hole acceptor mechanisms. The desensitisation *via* the electron acceptor mechanism — type I desensitisation — is induced by dyes, including infrachromatic dyes, with a high electron affinity. After the exposure of AgHal to light ($h\nu$), the desensitising dyes capture photoelectrons from the conduction band in the ϵ_{lv} levels lying below the bottom of the AgHal conduction band and thereby divert them from the formation of a latent photographic image (Fig. 3). Thus the condition for the type I desensitisation is $E_{1/2}^{\text{Red}}(\text{Dy}) > E_{\text{CB}}$. This process can be represented schematically as follows:



In this scheme, stage (4) corresponds to the irreversible loss of electrons as a result of the chemical interaction of $\text{Dy}^{\cdot-}$ with the components of the photographic emulsion. Stage (5) reflects the recombination of the electrons, captured by Dy , with AgHal holes.

An appreciable intensification of the desensitisation by electron-accepting dyes in the presence of oxygen and water was already noted comparatively long ago.^{18,27} Blau and Wambacher⁴² noted that the desensitising effect of Pinakryptol Yellow and phenosafranin is manifested only in the presence of oxygen. It was postulated that the desensitiser is more likely to be an oxidation 'transferring agent' than an oxidant proper. The influence of oxygen and moisture on emulsions containing electron-accepting dyes was also pointed out by Carrol and coworkers.⁴³

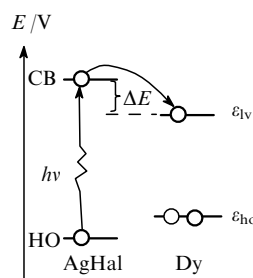


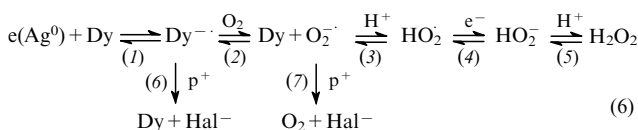
Figure 3. Schematic illustration of type I desensitisation.

The influence of oxygen and moisture on the sensitivity of spectrally sensitised emulsions was later confirmed in other studies.^{26,30,40,44–51} It has been suggested⁵¹ that the influence of oxygen on infrachromatic materials is associated with the formation of the complex $[\text{Dy} \cdot \text{O}_2]$. The studies of the influence of various emulsion factors, as well as the structure of dyes, on type I desensitisation processes have been thoroughly reviewed by Dühne.¹⁸

Considerable attention has been devoted to the role of oxygen and water in type I desensitisation processes in the communications of James and coworkers,^{26,27,48} in which electron transfer from the AgHal conduction band *via* the dye to O_2 with formation of the $\text{O}_2^{\cdot-}$ radical-anion is discussed. The special role of water in the irreversible binding of photoelectrons with formation of hydrogen peroxide is emphasised.⁴⁸

The following mechanism has now been adopted for type I desensitisation (Scheme 1).^{5,6,17,27}

Scheme 1



In the first stage of the desensitisation process, an electron from the AgHal conduction band or from a surface trap (in particular from the Ag^0 precentre of the latent image) is captured by the dye in the ground state, which is then converted into the $\text{Dy}^{\cdot-}$ radical-anion. Next the excess electron is transferred from $\text{Dy}^{\cdot-}$ to O_2 with formation of the $\text{O}_2^{\cdot-}$ radical-anion. The superoxide radical-anion $\text{O}_2^{\cdot-}$ is known to be readily protonated, affording the radical $\text{HO}_2^{\cdot}$ with a much higher electron affinity than O_2 .^{5,6} The radical $\text{HO}_2^{\cdot}$ therefore readily captures a second electron. The anion HO_2^- formed thereby is subsequently protonated, giving rise to hydrogen peroxide. In addition, there is a possibility of the recombination of the radical-anions $\text{Dy}^{\cdot-}$ and $\text{O}_2^{\cdot-}$ with holes (stages 6 and 7).

According to the above mechanism, the dye in the ground state plays the role of an intermediate, transferring electrons from the silver atom to O_2 and the water protons, *i.e.* one is dealing with catalysis by the dye of oxidation processes with participation of oxygen and protons. The transformation of the single-stage oxidation reaction into a series of consecutive reactions in each of which the activation energy for the process is smaller than in the single-stage reaction then leads (as in any catalytic processes) to the acceleration of the overall process.

The intermediate participation of the dye in electron transfer (stage 1) is determined by its electron affinity or, more specifically, by the depth (ΔE) of the ϵ_{lv} level of the adsorbed dye under the AgHal conduction band (Fig. 3). Furthermore, the effectiveness of the electron capture depends on the capture cross-section, which is a function of the charge and length of the dye molecule. Thus, other conditions being equal, the deeper the ϵ_{lv} level of the dye *i.e.* the smaller the absolute magnitude of $E_{1/2}^{\text{Red}}(\text{Dy})$, the greater should be the extent of desensitisation.

The relation between the desensitising effect of dyes and the position of their lowest vacant electronic level has been pointed out independently by Bogomolov and Moshkovskii,⁵³ by Tamura and Hada,^{54,55} and also by Sheibe and Dörr.^{56,57} The dependence of the desensitisation on the polarographic potentials $E_{1/2}^{\text{Red}}(\text{Dy})$ was first noted in the study of Sheppard *et al.*⁵⁸ The authors quote a potential of -0.70 V (relative to n.h.e.) or -0.92 V (relative to the Ag/AgCl electrode) as the upper limit for desensitisation. Later these values were confirmed.⁵⁹ The same limiting potentials have been quoted by Dähne.^{18,22,60} Desensitisation potentials in the range from -0.86 to -1.05 V (relative to the Ag/AgCl electrode) have been given in a number of studies.^{17,40,61–64} Thus, on average the boundary desensitisation potential on the polarographic potential scale is -1.0 V (relative to the Ag/AgCl electrode). The limiting potential depends on emulsion factors and primarily on pAg. With increase in pAg and also with increase in the dye concentration, an intensification of the desensitisation is observed.¹⁸

In vinylogical series of polymethine dyes, the desensitising effect increases with increase in the length of the polymethine chain, which agrees with the increased depth of the ε_{IV} level.^{15,18,65} The quantitative dependence of the desensitisation on the dye ε_{IV} has been investigated by Strurmer *et al.*⁶⁶ It was shown that the desensitisation steadily increases with increase in the depth of the ε_{IV} level.

The dependence of the degree of desensitisation on $E_{1/2}^{\text{Red}}(\text{Dy})$ has been examined in detail by Mikheeva *et al.*⁶⁷ The degree of desensitisation (SD) is understood as the ratio of the intrinsic sensitivity of the AgHal emulsion without the dye (S) to the sensitivity in the presence of the dye (S'):

$$SD = \frac{S}{S'}.$$

The linear dependence of $\lg SD$ on $E_{1/2}^{\text{Red}}(\text{Dy})$ of the general type

$$\lg SD = m E_{1/2}^{\text{Red}}(\text{Dy}) + n, \quad (7)$$

has been discovered.⁶⁷ Here m and n are constants for constant pAg and the dye concentration. Figs 4 and 5 illustrate the dependence of $\lg SD$ on $E_{1/2}^{\text{Red}}(\text{Dy})$ for different dye concentrations and different pAg. It is striking that the linear relation is retained over a definite range of pAg and concentrations, the slope of the curves increasing with increase in pAg and the dye concentration. The boundary desensitisation level is -1.1 V (relative to sat. c.e.).

The linear dependence of $\lg SD$ on $E_{1/2}^{\text{Red}}(\text{Dy})$ has been explained within the framework of the kinetic model of spectral sensitisation processes⁶⁷ on the basis of the electrochemical potentials of the dyes and other components of the photographic emulsion, which was developed in the present authors studies.^{5,6,17,23} The model is based on the Marcus theory of electron transfer in polar media.⁶⁸ Since the spectral sensitisation and desensitisation of AgHal are typical oxidation-reduction reactions occurring in a polar medium, the Marcus theory is fully applicable to them. According to the Marcus theory, there is a linear relation between the free energy of formation of the transition state ($\Delta G^\ddagger$) and the thermodynamic characteristics of the elementary oxidation-reduction step:

$$\Delta G^\ddagger = -RT \ln k \approx a \Delta G^0 + b \approx an F \Delta E^0 + b, \quad (8)$$

where k is the reaction rate constant, ΔG^0 the standard free energy change in the reaction, a and b are constants for a particular class of reactions, n is the number of electrons in the reaction, F the Faraday, and ΔE^0 the difference between the standard potentials.

In this case, the rate of electron transfer between the components of the photographic emulsion — the molecules of Dy^* , Dy , AgHal^* , AgHal , and other compounds — can be expressed by kinetic equations in which the activation energy is a function of the difference between the normal oxidation-reduction potentials of the systems participating in the electron transfers. For example, the rate of passage of electrons into the conduction band or onto the AgHal surface levels, which determines the light sensitivity of

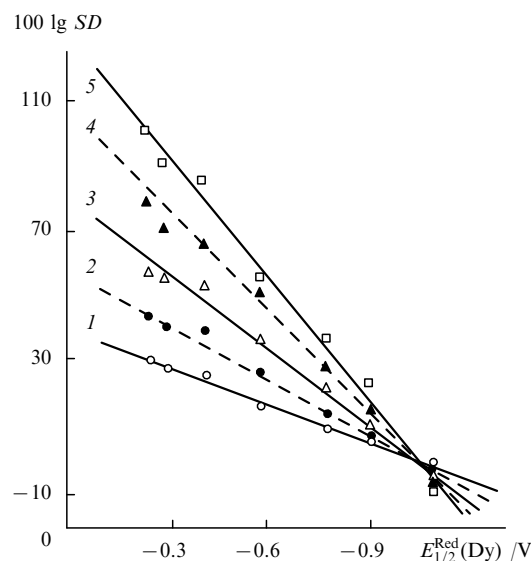


Figure 4. Dependence of $\lg SD$ on $E_{1/2}^{\text{Red}}$ at different dye concentrations $10^6 c_{\text{Dy}}$ (mol per mole of AgHal) (pAg 8.0): (1) 1; (2) 2; (3) 4; (4) 8; (5) 10.

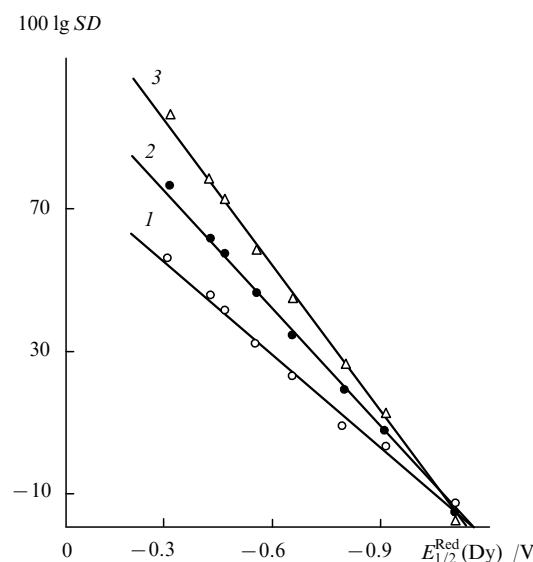


Figure 5. Dependence of $\lg SD$ on $E_{1/2}^{\text{Red}}$ at different pAg: (1) 7.4; (2) 8.0; (3) 8.9. Dye concentration 2×10^{-6} mol per mole of AgHal.

the negative process, can be expressed as the sum of the rates of electron flow in individual channels of the electron transfer reactions:

$$\sum_i \left(\frac{dn_{i(e)}}{dt} \right) = \sum_i k_i c_i = \sum_i A_i c_i \exp \left(- \frac{\alpha_i \Delta E_i^0}{T} \right), \quad (9)$$

where $n_{i(e)}$ is the number of electrons in the conduction band or on the AgHal surface, k_i the rate constant for electron transfer, c_i the concentration (or more precisely the activity) of the electron-donating (reduced) form of the i th system, formed after photoexcitation and capable of electron exchange with the conduction band or with the surface levels, A_i and α_i are constants for a particular class of reactions, and ΔE_i^0 is the difference between the normal potential of the i th system, formed after photoexcitation, and the potential of the bottom of the conduction band E_{CB}^0 or the electron-accepting levels ($E_{\text{SL}(e)}^0$).

The kinetics of electron capture from the conduction band by the components of the photographic emulsion may be expressed

as the sum of the rates of the reactions, one of which is the formation of the latent image:

$$\sum_j -\left(\frac{dn_{j(e)}}{dt}\right) = \sum_j k_j c_j n_{(e)} = \sum_j A_j c_j n_{(e)} \exp\left(-\frac{\alpha_j \Delta E_j^0}{T}\right), \quad (10)$$

where c_j is the concentration of the electron-accepting (oxidised) form of the j th system and ΔE_j^0 is the difference between the potential of the bottom of the conduction band E_{CB}^0 (or $E_{SL(e)}^0$) and the normal potential of the j th system. The photographic sensitivity is determined by the ratio of the rates of the reactions involving the migration of electrons into AgHal and their irreversible binding.^{5,17}

We shall now consider the desensitisation process. According to Scheme 1, the primary stage of the desensitisation process is the capture of electrons from the conduction band or from the surface traps by the dye in the ground state. Stage 1 may be rate-determining for the overall desensitisation process. The rate constant for the protonation of O_2^- (stage 3) is known to be nearly diffusional, i.e. equal to $10^{10} \text{ cm}^{-1} \text{ s}^{-1}$.⁶⁹ Stage 2 can also be fairly fast, since the normal potential of the O_2^-/O_2 system is -0.284 V (relative to n.h.e.),⁶⁹ i.e. is significantly more positive than $E_{1/2}^{\text{Red}}(\text{Dy})$ for the majority of dyes. If it is assumed that stage 1 is rate-limiting, then the rate of capture of electrons from the conduction band by the dye is determined according to Eqn (10) (for $c_{Dy} = \text{const.}$ and $n_e = \text{const.}$) by the difference between the potentials of the bottom of the conduction band E_{CB}^0 and $E^0(\text{Dy}^-/\text{Dy})$. For reversible systems, the potential $E^0(\text{Dy}^-/\text{Dy})$ is virtually identical with $E_{1/2}^{\text{Red}}(\text{Dy})$. The electron capture rate constant (stage 1 in Scheme 1) can be expressed in the form

$$k_1 = A_1 \exp\left(-\alpha_1 \frac{\Delta E_1^0}{T}\right), \quad (11)$$

where $\Delta E_1^0 = E_{CB}^0 - E_{1/2}^{\text{Red}}(\text{Dy})$. The degree of desensitisation at constant pAg should be proportional to k_1 , the concentration of electrons which have emerged onto the surface of AgHal microcrystals after passing through the conduction band (c_e), and the dye concentration (c_{Dy}):

$$SD \approx k_1 c_e c_{Dy}, \quad (12)$$

For constant pAg, c_e , and c_{Dy} , we have

$$SD \sim k_1 \sim \exp\left(-\frac{\Delta E_1^0}{T}\right) \sim \exp\left(-\frac{E_{1/2}^{\text{Red}}(\text{Dy})}{T}\right). \quad (13)$$

Indeed, according to Figs 4 and 5 there is a linear dependence of $\lg SD$ on $E_{1/2}^{\text{Red}}(\text{Dy})$.⁶⁷ It is noteworthy that the form of the dependence of $\lg SD$ on $E_{1/2}^{\text{Red}}(\text{Dy})$ does not change if electrons are captured by the dye not directly from the conduction band but from the surface electron traps (e_s). In this case, only ΔE_1^0 changes. It may be that electrons are captured both from the AgHal conduction band and from the surface traps.

Naturally, with increase in the concentration of the desensitiser dye, there is an increase in the rate of electron capture. This explains the relation, noted by Dähne,⁶⁰ between $\lg SD$ and the dye concentration (more precisely $\lg c_{Dy}$ — see Fig. 4). The dependence of $\lg SD$ on pAg is determined by the competition between the silver ions and the dye for electron capture from the conduction band. Furthermore, Ag^+ ions may capture electrons from Dy^- and O_2^- , formed in stages 1 and 2 (see Scheme 1), and hence can return them to the construction of the latent image. This explains the decrease in desensitisation with decrease in pAg (Fig. 5).

The quantity $E_{CB}^0 = -1.1 \text{ V}$ (relative to n.h.e.) or approximately -1.34 V (relative to sat. c.e.) for AgBr has been determined from experimental and calculated data.⁶⁷ Fig. 6 presents a diagram illustrating the normal oxidation-reduction potentials for the components of the silver halide emulsion. The potential diagram is extremely important methodologically, since it makes

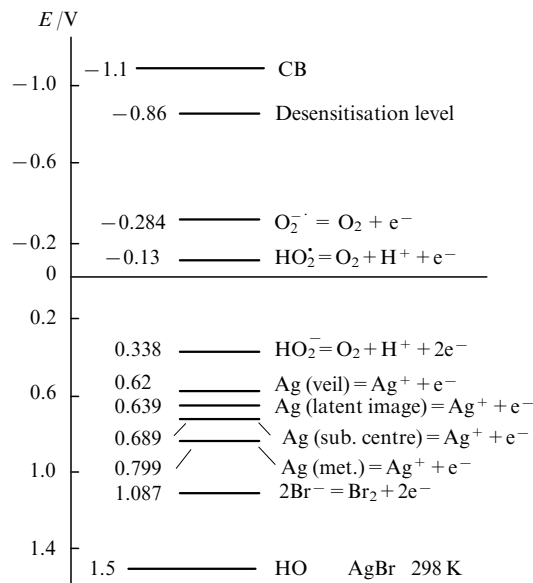


Figure 6. Oxidation-reduction potential diagram for the components of a AgHal emulsion.

it possible to compare the potentials of the electron bands of AgHal, the dyes, the photographically active silver particles, and various components of the photographic emulsion. As an example, Fig. 7 illustrates the type I desensitisation reaction path for a dye with $E_{1/2}^{\text{Red}}(\text{Dy}) = -0.6 \text{ V}$ (relative to n.h.e.).

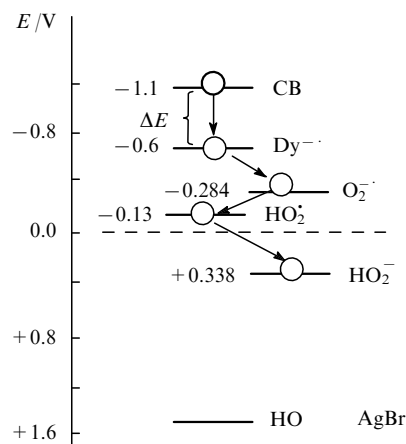


Figure 7. Energy scheme for a type I desensitisation process.

IV. Self-desensitisation of dyes

It is natural to postulate that secondary oxidative desensitisation processes should occur not only on photoexcitation of AgHal but also on photoexcitation of the dye itself — the spectral sensitiser. One is dealing with reactions involving the self-desensitisation of dyes,^{2, 5, 6, 23} which is understood as the desensitising influence of the spectral sensitiser on the photoprocess in the region of its absorption. In the literature, this process had been previously called selective desensitisation in the region of spectral sensitisation.^{27, 32, 70}

Unfortunately it is virtually impossible to estimate quantitatively the influence of the spectral sensitisers themselves on the spectral sensitivity, since one cannot carry out a control exposure in the same spectral zone without the dye. An indirect method is

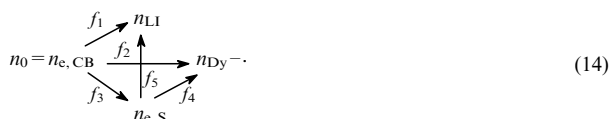
therefore used — the influence of an additionally introduced desensitiser on the spectral and intrinsic sensitivity is inferred, *i.e.* the selective desensitisation is estimated.

The difference between the desensitisation and selective desensitisation processes in the region of spectral sensitisation has been considered in a number of studies^{23, 27, 70} and the greater influence of the additionally introduced desensitisers on the spectral sensitivity compared with the intrinsic sensitivity was explained by the fact that, on photoexcitation of AgHal, desensitisation is achieved by the capture of electrons from both deep electron traps (light sensitivity centres) and from shallow surface traps. On the other hand, on photoexcitation of the dye, all the photoelectrons are initially transferred to shallow surface traps, from which the capture of electrons in vacant levels of the desensitising dye is facilitated and to a greater extent the higher the value of $E_{1/2}^{\text{Red}}(\text{Dy})$. In conformity with Scheme 1, the desensitisation increases the probability of stage 1 in this case, because the concentration of the electrons captured on the AgHal surface (e_s or Ag^0) is greater than on excitation of AgHal electrons into the conduction band, from which a large proportion of the electrons are immediately captured by the comparatively deep levels of the light-sensitivity centres.

The difference between the processes occurring on photoexcitation of AgHal and the dye has been inferred⁷¹ from the amplitude and the relaxation time of the photo-e.m.f. of AgBr(1) emulsions with sulfur sensitisation. The smaller decrease in the amplitude of the photo-e.m.f. during sulfur sensitisation in the region of spectral sensitivity compared with the region of the intrinsic absorption of AgHal was explained by the fact that the impurity centres formed on chemical sensitisation capture more effectively the electrons generated in the bulk of the microcrystals than the photoelectrons formed on photoexcitation of the dye. The latter are initially captured by centres on the AgHal surface and only then pass into the conduction band. The longer growth and relaxation times the photo-e.m.f. in the region of spectral sensitisation than in the region of the intrinsic absorption of AgHal are associated with this fact.⁷²

The influence of electron acceptors — pyrylocyanines with a variable electron affinity characterised by $E_{1/2}^{\text{Red}}(\text{Dy})$ — on the degree of desensitisation SD and the degree of desensitisation SD_λ in the region of spectral sensitivity of emulsions spectrally sensitised by thiocyanines has been studied in detail.⁶⁷ Fig. 8 presents the dependence of $\lg SD$ and $\lg SD_\lambda$ on $E_{1/2}^{\text{Red}}(\text{Dy})$ of the desensitisers for a coarse-grain AgBr(1) emulsion with S + Au sensitisation, containing thiadi- and thiatricarbocyanines as spectral sensitisers. It follows from Fig. 8 that the slope of the $\lg SD = f(E_{1/2}^{\text{Red}})$ relations is significantly greater than that of the $\lg SD = f(E_{1/2}^{\text{Red}})$ relations, *i.e.* the influence of desensitisers on the additional sensitivity is more marked.

On desensitisation, the fate of the n_0 electrons formed in the conduction band ($n_{e,\text{CB}}$) on photoexcitation of AgHal can be represented by the following scheme:⁶⁷



Some of the electrons (f_1) migrate to the sensitivity centres and form the latent image (n_{LI}) others (f_2) are captured directly by the dye (n_{Dy^-}) and are lost in accordance with Scheme 1, while a third part of the electrons (f_3) initially migrate to other surface traps ($n_{e,s}$), a proportion of which (f_4) are captured by the dye while another fraction (f_5) may be thermally excited into the conduction band and can be used in the construction of the latent image. Thus $n_0(f_2 + f_3f_4)$ electrons are diverted from the construction of the latent image. In this case,

$$SD = \frac{n_0}{n_0 - n_0(f_2 + f_3f_4)} = \frac{1}{1 - f_2 - f_3f_4} = \frac{1}{f_1 + f_3f_5}. \quad (15)$$

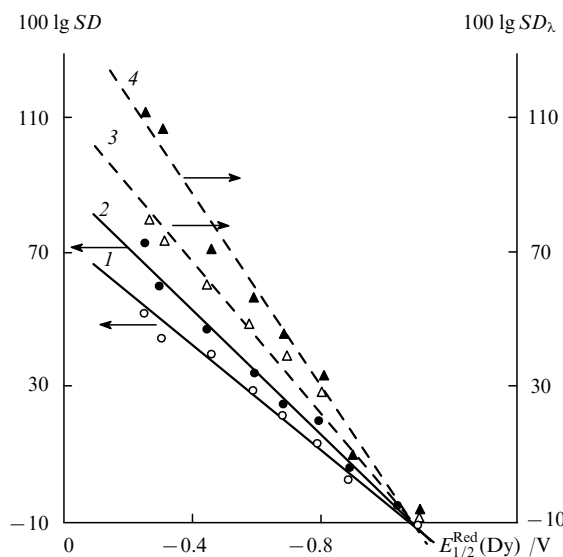
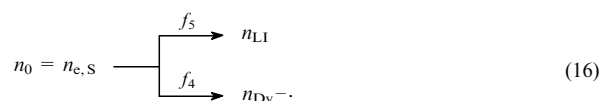


Figure 8. Dependence of $\lg SD$ (1, 2) and $\lg SD_\lambda$ (3, 4) on $E_{1/2}^{\text{Red}}$ for emulsions sensitised by 3,3'-diethylthiadicarbocyanine iodide (1, 3) and 3,3'-diethylthiatricarbocyanine iodide (2, 4). Dye concentration 2×10^{-6} mol per mole of AgHal (pAg 8.0).

When the quantities f_2 and f_3 are small compared with f_1 , $SD = 1$ and $\lg SD = 0$.

If it is postulated that, on structural sensitisation, all n_0 electrons initially migrate to surface traps, then the scheme according to which electrons are distributed becomes different:



In this case,

$$SD_\lambda = \frac{1}{1 - f_4} = \frac{1}{f_5}. \quad (17)$$

It follows from Eqns (15) and (17) that

$$\frac{SD_\lambda}{SD} = \frac{1 - f_2 - f_3f_4}{1 - f_4} = \frac{f_1 + f_3f_5}{f_5}. \quad (18)$$

Since usually $f_1 > f_5$ in the presence of a desensitiser, we have $SD_\lambda/SD > 1$. On the other hand, the contributions of f_2 and f_4 diminish exponentially with decrease in $E_{1/2}^{\text{Red}}$ of the dye:

$$f_2(f_4) \sim \exp\left(\frac{E_{1/2}^{\text{Red}}}{RT}\right),$$

Therefore, at a certain limiting potential $E_{1/2}^{\text{Red}}$ where f_2 and f_4 tend to zero, we have $SD_\lambda/SD = 1$. This corresponds to the observed critical potential $E_{1/2}^{\text{Red}} = -1.1$ V at which the $\lg SD = f[E_{1/2}^{\text{Red}}(\text{Dy})]$ and $\lg SD_\lambda = f[E_{1/2}^{\text{Red}}(\text{Dy})]$ curves intersect (Fig. 8).

$$\Delta \lg SD = (\lg SD_\lambda - \lg SD) \sim [E_{1/2}^{\text{Red}}(\text{Dy}) - 1.1]. \quad (19)$$

Thus the difference between SD and SD_λ can be explained within the framework of the above scheme governing the transition of electrons from Dy^* to surface levels by the difficulty of the direct electron transfer to sensitivity centres on spectral sensitisation. Such transfer requires an additional energy for the excitation of electrons into the conduction band. In the absence of such energy, the probability of the capture of electrons from surface traps by the dye increases. According to Eqn (19), the difference between SD and SD_λ increases with increase in $E_{1/2}^{\text{Red}}(\text{Dy})$.

The same type of dependence of SD and SD_λ on $E_{1/2}^{\text{Red}}(\text{Dy})$ (Figs 4, 5, and 8) suggests that the self-desensitisation by the spectral sensitisers themselves, possessing an electron affinity, is fully realistic and may at the same time significantly exceed the desensitisation, particularly at elevated concentrations of dyes. The marked dependence of the spectral sensitivity of infrared emulsions on the concentration of the sensitiser compared with the intrinsic sensitivity is well known. It follows from Fig. 9 that the decrease in spectral sensitivity observed at certain dye concentrations is more abrupt than the decrease in the 'blue' sensitivity of AgHal. The effective self-desensitisation then requires, like desensitisation, the presence of oxygen and moisture in the light-sensitive layer. This has been confirmed by the observation⁷³ of an increase in the spectral sensitivity of infrachromatic layers *in vacuo* and in a moist atmosphere without oxygen whereas the simultaneous presence of oxygen and water suppressed sharply the sensitivity. The influence of water on the sensitivity of infrachromatic ultrafine-grain AgBr emulsions has been investigated.⁷⁴ It was shown that the increase in the spectral sensitivity

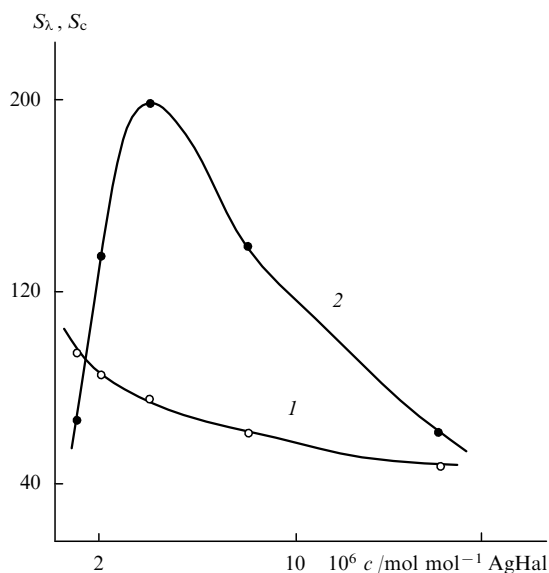


Figure 9. Dependence of the intrinsic light sensitivity S_i (1) and additional light sensitivity S_λ (2) of an emulsion sensitised by 3,3'-diethylthiadicarbocyanine iodide on the dye concentration (pAg 8.0).

of the emulsions after their drying is greater the higher the values of $E_{1/2}^{\text{Red}}(\text{Dy})$ and pAg. The influence of an electron-accepting dye on the lifetime of the silver precentres of the latent image in the presence of oxygen and moisture has been convincingly demonstrated in a study⁷⁵ where a sharp decrease in the lifetime of the precentres under the influence of a desensitising dye (phenosafranin) was observed. The regression of the latent image on an emulsion with sulfur sensitisation under the influence of a series of infrared dyes has been investigated.^{6, 76} According to the results presented in Fig. 10, electron-accepting dyes accelerate significantly the regression of the latent image in conformity with Scheme 1.

The contribution of the dye self-desensitisation processes depends to a significant extent on the type of the AgHal emulsion. The decrease in self-desensitisation on emulsions of the 'core-shell' type and on an emulsion with Ir^{3+} ions in the bulk of the microcrystals may be a consequence of the lower probability of the oxidation of the latent image precentres as a result of the rapid electron transfer from these centres into the bulk of the microcrystals — onto the subsurface electron acceptance centres. This is equivalent to a decrease in the fraction of the electrons f_5 in Eqn (17). This property of the 'core-shell' emulsions and emulsions

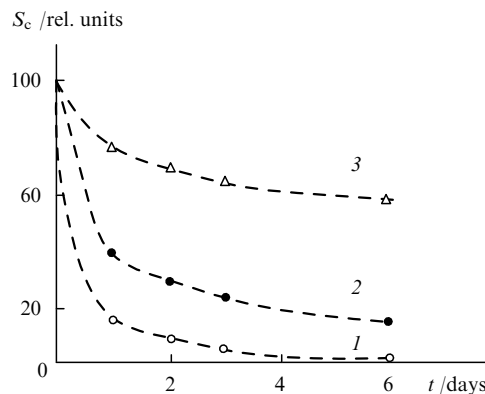


Figure 10. Variation of the intrinsic sensitivity S_i of photographic emulsions sensitised by thiapentacarbocyanine (1) and thiatetracarbocyanine (2) and in the absence of dyes (3) at 35 °C and 100% humidity. Dye concentration 1.8×10^{-4} mol per mole of AgHal.

with Ir^{3+} has in fact made it possible to increase significantly the concentration of spectral sensitisers and the efficiency of the spectral sensitisation itself.^{37, 77–81} The decrease in the desensitisation of dyes in the region of their spectral sensitisation on a 'core-shell' emulsion has been demonstrated.⁶⁷

As a result of the examination of the role of dye self-desensitisation processes in the establishment of spectral sensitivity, it was concluded²³ that the self-desensitisation of dyes can in essence determine the effectiveness of the spectral sensitisation itself. From this it follows that the main problem in raising the effectiveness of spectral sensitisation is that of the inhibition of the secondary dye self-desensitisation reactions.

V. Supersensitisation processes as inhibition of the self-desensitisation of dyes

There are methods for increasing the spectral sensitivity of photographic emulsions sensitised by dyes with a low level of the photoexcited electron [$E_{1/2}^{\text{Red}}(\text{Dy}) > -1.0$ V], including infrachromatic dyes.^{2, 5, 82, 83} These methods known under the general term of supersensitisation, can be considered from a single standpoint of dye self-desensitisation processes within the framework of Scheme 1.^{5, 6}

For the inhibition of stage 1 (Scheme 1), the dye molecules must be separated from the AgHal surface on the defects of which electrons from Dy^* may be captured. One is dealing with a kind of insulation of dye molecules from AgHal, which, however, must not prevent the electron transfer from Dy^* , i.e. a 'spacer' sufficiently permeable to photoexcited electrons and impermeable to electrons captured by traps on the AgHal surface must be created between the dye and AgHal. One can postulate *a priori* that organic substances readily adsorbed on AgHal are needed for the creation of spacers between AgHal and the dye. Such insulation is important also from the standpoint of the elimination of reactions involving the recombination of electrons with the dye radical-cations formed in the spectral sensitisation step. It may be that the separation of the dye not from the entire AgHal surface but only from the photographically active centres, where photoelectrons are located, plays an important role. In this case, the role of the organic spacers is the same as that of the AgHal shells in emulsions of the 'core-shell' type or in emulsions with deep electron capture centres created by Ir^{3+} ions.

It is essential to note that the problem of the effective charge separation in a photochemical reaction, including separation owing to the decrease in the reverse recombination of charges with the aid of the so called membranes, is general and constitutes one of the principal problems of sensitised photolysis, in particular the sensitised photolysis of water.^{84, 85}

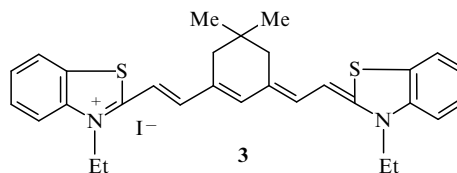
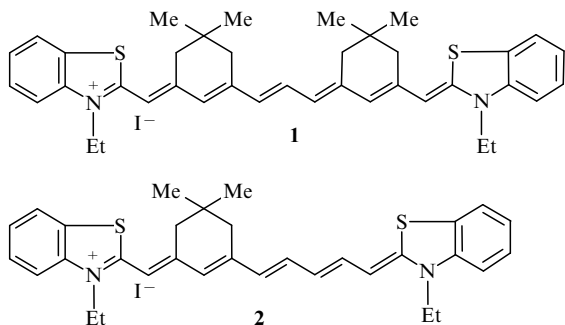
The inhibition of stages 2–5 (Scheme 1) by the insulation of the dye molecules from oxygen and water with the aid of hydrophobic organic compounds, introduced in the stage involving the preparation of photographic emulsions, is also extremely promising.^{5,23,86} Such compounds should not be adsorbed on AgHal, but, on introduction into a water–gelatin emulsion, they should be deposited on the AgHal microcrystals owing to their hydrophobic nature and create a kind of shell protecting the dye from oxygen and water.

The use of substances adsorbable on AgHal as supersensitisers for photographic materials is well known. Riester^{87,88} showed that, when a series of sulfomercapto-derivatives of heterocyclic bases are introduced, certain dyes, including azomethine dyes, which are relatively ineffective and even desensitising under the usual conditions, become effective spectral sensitisers. According to Riester's 'glue' model, the supersensitisers (potentiators) are attached with the aid of the mercapto-group to the Ag⁺ ions on the surface of microcrystals, while the sulfo-groups interact with the positively charged dye chromophores with formation of salt-like products, retaining thereby the dye molecules at a certain distance from AgHal (vaulted structure). The formation of this type of structure of the adsorbed dye promotes, according to Riester, a more effective excitation energy or electron transfer from Dy* to AgHal and also a decrease in desensitisation as a result of the capture of photoelectrons by the dye. This agrees with the conclusions reached by O'Brien,⁸⁹ who believes that the sensitisation efficiency is greater when the dye is fixed at a distance of 10–20 Å above the AgBr surface.

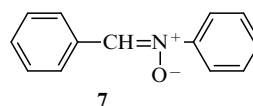
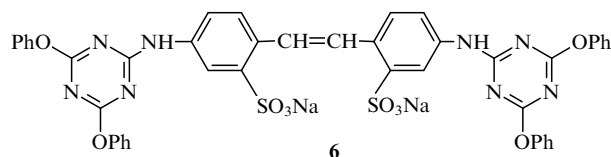
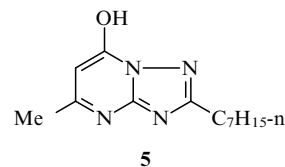
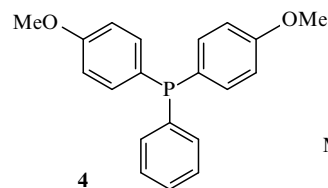
Carrol and Johnson⁹⁰ and also Vompe and coworkers^{91,92} described the supersensitising effect of bistriazinylamino-derivatives of stilbene-*o,o'*-disulfonic acid on infrachromatic dyes. The alkyl derivatives of 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene (for example, the 2-heptyl derivative)^{93,94} and various triaryl-phosphines^{95–98} also exert supersensitising and antifogging effects.

It is essential to note that Gilman's supersensitisation mechanism,⁸² adopted in the literature, the operation of which requires that the supersensitiser should be oxidised more readily than the dye, is inapplicable in this instance, since supersensitisers of the above type are as a rule more difficult to oxidise than the dyes.⁸³ Thus the mechanism of the action of supersensitisers of this type on infrachromatic emulsions is obscure and the search for the latter is purely empirical. However, it is striking that the above compounds are adsorbed on AgHal^{99,100} and may therefore play the role of 'insulators' between the dye and AgHal.

As an illustration of the action of supersensitisers of different structures, we shall present data obtained on an ultrafine-grain ($d = 0.05 \mu\text{m}$) transparent AgBr(I) emulsion.^{101,102} The use of a transparent emulsion makes it possible to measure the absorption spectra of light-sensitive layers in the IR region. The emulsion was sensitised by penta-, tetra-, and tri-carbocyanine dyes with structures **1**, **2**, and **3**.



Di-(*p*-anisyl)phenylphosphine **4**, 2-heptyl-4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene **5**, the disodium salt of *p,p'*-bis(4,6-diphenoxo-1,3,5-triazin-2-yl-amino)stilbene-*o,o'*-disulfonic acid **6**, and *C,N*-diphenylnitron **7** were used for supersensitisation. The supersensitisers **4–6** are compounds adsorbable on AgHal, while the nitron **7** is weakly adsorbable.



In the first place, it was shown in experiments without supersensitisers that the intensity of the principal bands of the dyes depends on pAg: with decrease in pAg, the absorption and the stability of the adsorbed dye increase.^{5,102} This is manifested particularly clearly on the pentacarbocyanine **1**. It follows from Fig. 11a that an appreciable increase in absorption by the dye occurs when pAg changes from 7.6 to 5.6, whereupon the absorption band maximum undergoes a hypsochromic shift. The increase in absorption and in the stability of the dye when a fused emulsion is allowed to stand may be attributed to the formation of complexes of the type $[\text{Dy} \cdot \text{Ag}_2^+]$ on the AgHal surface.^{23,83,103} This may be the cause of the hypsochromic shift of the absorption band, since the polymethine structure of the dye should be disturbed with a consequent hypsochromic shift of the absorption on formation of a bond between a methine carbon atom of the chain and Ag_2^+ . The stabilisation of the dye is also induced by the Ti^+ , Cd^{2+} , Pb^{2+} , Bi^{3+} , Al^{3+} , and Th^{4+} cations. It is striking that, with increase in the charge on the cation, the concentration of the compound which leads to an increment in the absorption by Dy and in the stabilisation of the latter diminishes steadily.¹⁰⁴ The stabilising effect of inorganic cations is associated with the formation of the complexes $[\text{Dy} \rightarrow \text{M}^{n+}/\text{AgHal}]$ on the AgHal surface, as a result of which there is a decrease in the probability of the donor–acceptor interaction of the adsorbed dye with the components of the dispersion medium (water, gelatin, etc.), resulting in the decolorisation of the dye.¹⁰³

With decrease in pAg, the spectral sensitivity S_λ increases (Fig. 11b) and, with increase in the wavelength of the absorbed light, the increase in spectral sensitivity becomes more marked (the 'fan' effect). Owing to experimental limitations, measurements at the sensitisation maximum have not been made. The increment in the long-wavelength sensitivity exceeds, even after correction for the increase in the intrinsic sensitivity of the emulsion, the increment in adsorption. A similar picture has been observed for the tetra- and tri-carbocyanines **2** and **3**.¹⁰²

The introduction of compounds **4** and **7** and their mixture into an emulsion with the pentacarbocyanine **1** also induces an increase

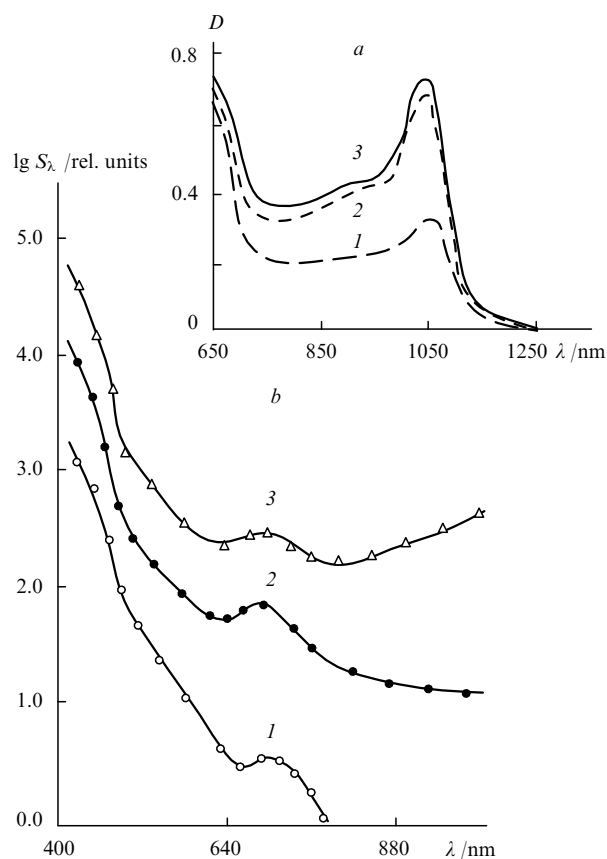


Figure 11. Absorption spectra (*a*) and spectral sensitivity curves (*b*) for emulsions sensitised by dye **1** at different pAg: (1) 7.6; (2) 5.6; (3) 4.6. Dye concentration — 2×10^{-4} mol per mole of AgHal.

in absorption and in the spectral sensitivity of the light-sensitive layers (Fig. 12). It is striking that di(*p*-anisyl)phenylphosphine causes a bathochromic shift of the dye absorption band (Fig. 12*a*). The increase in spectral sensitivity is illustrated in Fig. 12*b*. An analogous picture of the growth of absorption and sensitivity following the introduction of supersensitisers has been observed for emulsions sensitised by tetra- (Fig. 13) and tri-carbocyanines (Fig. 14). Like compound **4**, compounds **5** and **6** induce a bathochromic shift of the principal absorption band of the dye. The results of the supersensitising effects of the additives **4**–**7** are summarised in Table 1.

The observed increment in the additional sensitivity under the influence of supersensitisers in most cases exceeds the increment in absorption. Thus the action of these compounds is to some extent analogous to the action of silver ions (pAg) noted above. It is noteworthy that the addition of supersensitisers induces an increase in the intrinsic sensitivity (for dyes **1** and **2**, owing to the decrease in the desensitisation of the dyes). After correction for the intrinsic sensitivity, the supersensitising effect of the additives **4**–**6** is manifested in all the cases listed in Table 1, while compound **7** has an effect only in a certain range of pAg (see experiments 2, 5, 9, and 14 in Table 1).

The increase in absorption and partly also the increase in sensitivity in the presence of supersensitisers are apparently associated with the increase in the adsorption and stability of the adsorbed dye. This can be accounted for by the decrease in the donor–acceptor interaction of the adsorbed dye with the components of the dispersion medium (water, gelatin, etc.) and by the insulation of the reaction centres of the dyes by organic (including hydrophobic) compounds.¹⁰³ This question will be examined below.

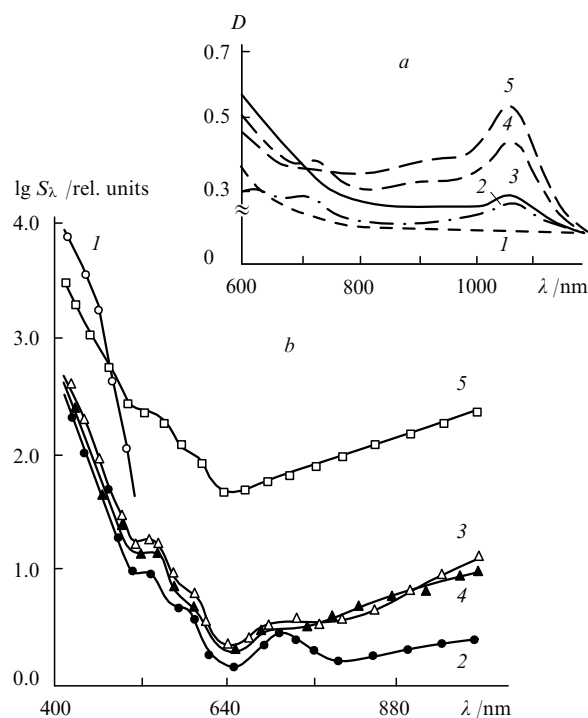


Figure 12. Absorption spectra (*a*) and spectral sensitivity curves (*b*) for emulsions without a dye (1), with dye **1** (2), and with dye **1** in the presence of supersensitisers **7** (3), **4** (4), and **4** + **7** (5) at pAg 5.6. Concentration of dye **1** — 4×10^{-4} mol per mole of AgHal and concentration of supersensitisers — 1×10^{-2} mol per mole of AgHal.

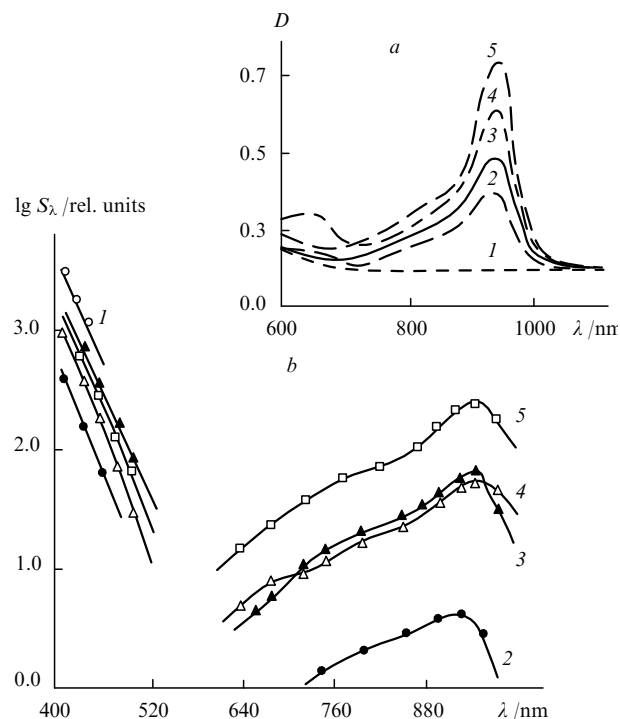


Figure 13. Absorption spectra (*a*) and spectral sensitivity curves (*b*) for emulsions without a dye (1), with dye **2** (2), and with dye **2** in the presence of supersensitisers **7** (3), **5** (4), and **7** + **5** (5) at pAg 7.6. Concentration of dye **2** — 2×10^{-4} mol per mole of AgHal and concentration of supersensitisers **5** and **7** — 3×10^{-3} and 1×10^{-2} mol per mole of AgHal.

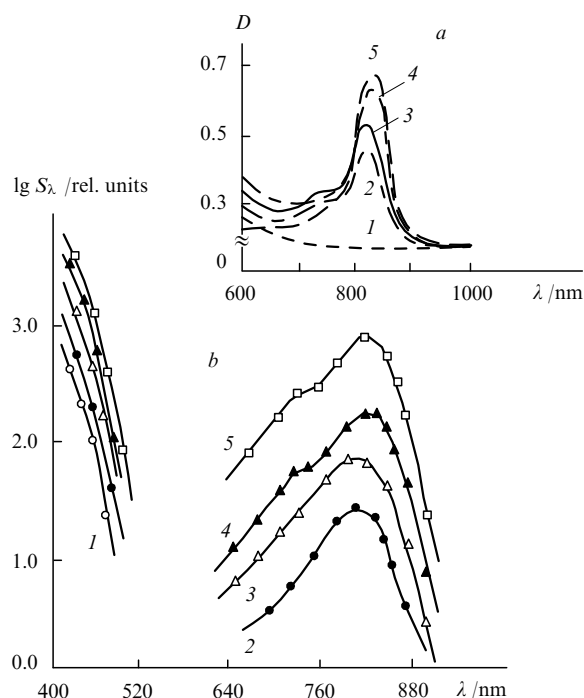


Figure 14. Absorption spectra (*a*) and spectral sensitivity curves (*b*) for emulsions without a dye (*1*), with dye **3** (*2*), and with dye **3** in the presence of supersensitisers **7** (*3*), **6** (*4*), and **6** + **7** (*5*) at pAg 9.0. Concentration of dye **3** — 2×10^{-4} mol per mole of AgHal and concentration of supersensitisers **6** and **7** — 1×10^{-2} mol per mole of AgHal.

Table 1. The influence of supersensitisers (S) on the absorption and light sensitivity of infrared light-sensitive layers.

No. of experiment	Dye	S	λ / nm	pAg	$\frac{D(\text{Dy} + \text{S})}{D(\text{Dy})}$ (see ^a)	$\frac{S_{\lambda}(\text{Dy} + \text{S})}{S_{\lambda}(\text{Dy})}$ (see ^b)	$\frac{nS_{\lambda}(\text{Dy} + \text{S})}{S_{\lambda}(\text{Dy})}$ (see ^c)
1	1	4	980	7.6	see ^d	13	4.8
2	1	7	980	7.6	see ^d	1.6	0.6
3	1	4+7	980	7.6	see ^d	32	9.5
4	1	4	980	5.6	4.0	4.3	3.8
5	1	7	980	5.6	1.7	4.6	3.6
6	1	4+7	980	5.6	5.7	100	11
7	2	4	935	9.0	12	93	40
8	2	5	935	9.0	7.0	8.9	5.6
9	2	7	935	9.0	4.3	2.5	0.4
10	2	4+7	935	9.0	13	590	47
11	2	5+7	935	9.0	15	710	83
12	2	4	935	7.6	1.9	11	7.1
13	2	5	935	7.6	2.1	15	12
14	2	7	935	7.6	1.5	13	5.9
15	2	4+7	935	7.6	2.3	83	22
16	2	5+7	939	7.6	2.7	63	19
17	3	6	825	9.0	1.6	7.1	2.0
18	3	7	825	9.0	1.2	2.8	1.2
19	3	6+7	825	9.0	1.7	28	6.6

^a Ratio of the optical densities of photographic emulsions with a dye and a supersensitiser and with the dye alone. ^b Ratio of the spectral sensitivities of photographic emulsions with a dye and a supersensitiser and with the dye alone. ^c Correction introduced to take into account the intrinsic sensitivity of AgHal (S_{420}); $n = S_{420}(\text{Dy})/S_{420}(\text{Dy} + \text{S})$. ^d For experiments 1–3, the values of *D* are not quoted because they are very low.

It is necessary to deal in greater detail with the effect of supersensitiser compositions. The compositions are responsible for a greater increase in absorption than the individual supersensitisers. This increase is in a number of instances close to the additive value or less than that (Table 1). On the other hand, the increment in additional sensitivity, even after correction for ΔS_{420} is in many instances superadditive, *i.e.* exceeds (sometimes considerably) the sum of the effects due to the individual supersensitisers. Superadditivity is manifested particularly clearly at high values of pAg (pAg 9.0 for dye **2** and pAg 7.6 for dye **1**). Thus the increase in the additional sensitivity greatly exceeds the increment in the absorption by the emulsions. It is striking that the use of compositions consisting of supersensitisers **4–6** does not induce a superadditive effect. Such an effect is observed only when these supersensitisers are employed together with the nitron **7**.

Since the supersensitisers alter only slightly the position of the absorption maximum due to the adsorbed dyes, one may conclude that these compounds hardly affect the positions of the energy levels of the dyes. The existence of a superadditive effect for compositions comprising supersensitisers of two types — adsorbed (compounds **4–6**) and weakly adsorbed (compound **7**) on AgHal⁹⁹ — constitutes definite evidence for the different mechanisms of the action of these compounds.

Special mention should be made of the fact that the relative quantum yield of the spectral sensitisation (ϕ_r^{420}) for light-sensitive layers containing the pentacarbocyanine **1** and the **4** + **7** composition (pAg 5.6) in the region of $\lambda = 1000$ nm is 0.14.⁵ This value is only a few times smaller than the yields ϕ_r^{420} for fine-grain photographic materials sensitised towards visible light despite the twofold decrease in the active light quantum.

The superadditive effect of the **4** + **7** and **5** + **7** supersensitiser compositions has been investigated in greater detail on a coarse-grain ($d = 1 \mu\text{m}$) highly sensitive AgBr(1) emulsion sensitised by the pentacarbocyanine **1** at pAg 7.2 and 7.8.¹⁰⁵ The supersensitisation was investigated over a wide range of light-sensitive layer exposure times — 10^2 – 10^{-11} s. For times of the order of 10^{-5} – 10^{-11} s, a YAG : Nd laser with $\lambda = 1060$ nm was used for the exposure, while for times of 5×10^{-2} – 1.6×10^2 s the emulsions were exposed in a FSR-41 sensitometer behind an interference light filter with $\lambda = 1050$ nm. The supersensitisation coefficient (*K*) was characterised by the ratio of the spectral sensitivity of the emulsion with the given supersensitiser (or with a supersensitiser composition) to the light sensitivity of the emulsion without supersensitisers. The results of these studies are presented in Table 2.

It follows from Table 2 that the introduction of supersensitisers into spectrally sensitised light-sensitive layers leads to an

Table 2. Dependence of the infrared emulsion supersensitisation effect on the supersensitisers employed and on the duration of exposure.

No. of experiment	Exposure time / s	pAg 7.2				
		<i>K</i> ₄	<i>K</i> ₅	<i>K</i> ₇	<i>K</i> ₄₊₇	<i>K</i> ₅₊₇
1	1.6×10^2	10	6.0	6.0	33	25
2	9	11	7.0	8.5	50	26
3	5×10^{-2}	16	10	14	120	50
4	10^{-5}	17	7.0	10	100	50
5	1.2×10^{-8}	15	6.0	10	100	50
6	3×10^{-11}	12	4.0	8.5	125	60
7	1.6×10^2	10	10	8.0	70	70
8	9	13	10	12	100	70
9	5×10^{-2}	16	11	14	160	180
10	10^{-5}	16	10	6.0	200	100
11	1.2×10^{-8}	20	12	7.0	250	110
12	3×10^{-11}	17	8.0	4.5	330	170

appreciable increase in sensitivity, but the degree of supersensitisation is different under these conditions: the greatest supersensitisation effect is observed for di-(*p*-anisyl)phenylphosphine **4**. A superadditive effect is characteristic of supersensitiser compositions, especially at pAg 7.8. The highest degree of supersensitisation has been determined for the **4** + **7** composition. It is striking that the coefficient K changes comparatively little (not more than by a factor of 2–3) over a wide range of exposure times, covering 13 orders of magnitude. This is possible if the supersensitisers have little effect on the primary step of the photochemical reaction and their action is manifested on slower secondary stages of the process involving the formation of the latent photographic image.

The results obtained for mixtures of supersensitisers are of special interest. The coefficients of supersensitisation by compositions greatly exceed the sum of the coefficients for the individual compounds and in certain cases are almost equal to or even exceed the product of the parameters for the individual substances (Table 2). Similar results have been obtained for a monodisperse AgBr(l) emulsion with cubic microcrystals ($l = 0.25 \text{ m}$).⁷⁶

As already mentioned, the superadditive effect of compositions may be a consequence of the different mechanisms of the action of the compounds constituting the composition and the fact that in most cases the coefficients are closer to the product than to the sum of the individual parameters can be regarded as a result of the supersensitising effect of the substances in the consecutive stages of the self-desensitisation process presented in Scheme 1. Since compound **7** does not possess a specific affinity for AgHal and is poorly adsorbed on the latter,⁹⁹ microcrystals and it most probably inhibits the self-desensitisation in stages 2–4 and 7 by insulating the dye molecules from oxygen and water. Thus its effect is similar to that of evacuation.^{23,83} The nitron is a hydrophobic compound, so that, after its introduction into a water–gelatin emulsion, it can be deposited on the AgHal may generate a kind of shell around them, promoting thereby the removal of oxygen and water from the surface of the crystal. The supersensitising effect of compounds **4**, **5**, and **6** may be associated with the inhibition of stage *I*, i.e. when adsorbed on AgHal,^{99,100} these compounds may separate the dye from AgHal and hence prevent the capture of electrons. One cannot rule out also a decreased probability of the direct electron transfer from Dy* to the dye in the ground state under the influence of these compounds.¹⁰⁶

The different effects of supersensitisers are schematically illustrated in Fig. 15, where it is shown that one supersensitiser (S-1) separates the dye from AgHal and the impurity centres formed in the course of chemical sensitisation, whilst the other (S-2) creates a shell insulating the dye from the medium.^{5,6}

We shall now consider the result of the effect of the supersensitiser composition assuming that the supersensitisers inhibit the electron loss reactions in two consecutive stages (for example, in stages 1 and 2 of Scheme 1) of the dye self-desensitisation process. The transfer of electrons from AgHal to the desensitiser D (for example to O₂) mediated by the dye is shown schematically in the same Fig. 15. Here f_1 is the designation of the fraction of electrons lost in the presence of the dye, $f_1 f_2$ represents the fraction of electrons lost in the presence of the dye and the supersensitiser S-1 separating the dye from AgHal, $f_1 f_3$ is the fraction of electrons in the presence of the dye and the supersensitiser S-2 separating the dye from the desensitiser D, and $f_1 f_2 f_3$ designates the fraction of electrons in the presence of the dye and the two supersensitisers S-1 + S-2 subject to the condition that the supersensitisers inhibit the loss of electrons in two consecutive stages.

If the light sensitivity of the photographic emulsion (S) is proportional to the number of electrons remaining on AgHal and forming the latent photographic image, then the supersensitisation coefficients can be formulated as follows:

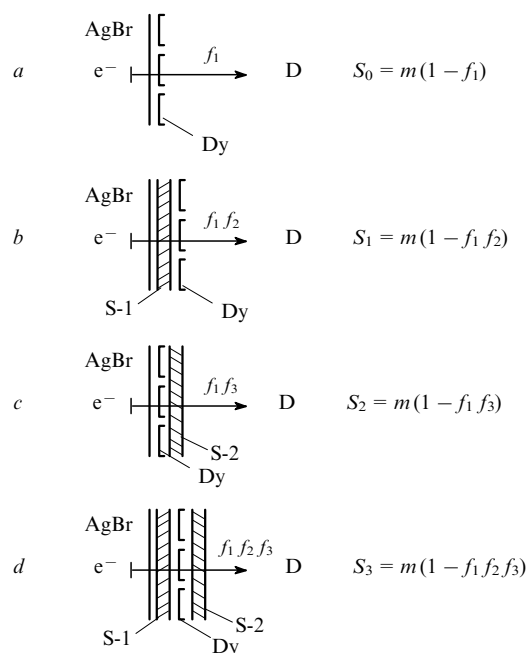


Figure 15. Schematic illustration of the processes involving the supersensitisation of photographic emulsions spectrally sensitised by a dye (a), by individual organic supersensitisers S-1 (b) and S-2 (c), and by the S-1 + S-2 composition (d).

$$K_1 = \frac{S_1}{S_0} = \frac{1 - f_1 f_2}{1 - f_1}, \quad (20)$$

$$K_2 = \frac{S_2}{S_0} = \frac{1 - f_1 f_3}{1 - f_1},$$

$$K_3 = \frac{S_3}{S_0} = \frac{1 - f_1 f_2 f_3}{1 - f_1}.$$

We shall consider several limiting cases:

1. $K_3 = K_1 K_2$.

We find from Eqns (20)

$$K_1 K_2 = \frac{(1 - f_1 f_2)(1 - f_1 f_3)}{(1 - f_1)(1 - f_1)} = \frac{1 - f_1 f_3 - f_1 f_2 + f_1^2 f_2 f_3}{(1 - f_1)^2}. \quad (21)$$

We adjust the quantities $K_1 K_2$ and K_3 to a common denominator:

$$K_3 = \frac{1 - f_1 f_2 f_3 - f_1 + f_1^2 f_2 f_3}{(1 - f_1)^2}. \quad (22)$$

Hence it follows that $K_3 = K_1 K_2$ if $f_2 + f_3 - f_2 f_3 = 1$. This is possible if the coefficients f_2 and f_3 or one of them are close to 1. In the latter case, one of the supersensitisers is appreciably less effective than the other.

2. $K_3 < K_1 K_2$

This case holds if $f_2 + f_3 - f_2 f_3 < 1$ or f_2 and $f_3 < 1$. This is a real case if both supersensitisers are active.

In the most general case where several (i) photosensitisers operate consecutively, we have

$$K_{i(i \rightarrow \infty)} = K_{\max} = \frac{1 - f_1 f_2 \cdots f_i}{1 - f_1} = \frac{1}{1 - f_1}, \quad (23)$$

i.e. the limiting value of the supersensitisation coefficient is determined by f_1 . If $f_1 = 0.9$ then $K_{\max} = 10$ and, if $f_1 = 0.99$, we have $K_{\max} = 100$. The last value is close to those obtained for the **4** + **7** supersensitiser composition at pAg 7.2 (Table 2).

3. $K_3 > K_1 K_2$

This case occurs for $f_2 + f_3 - f_2 f_3 > 1$ or for f_2 and $f_3 > 1$. It is unrealistic, because the number of electrons lost exceeds the number present initially.

If it is assumed that the light sensitivity of emulsions with the 4 + 7 supersensitisers is close to the limiting value and that the supersensitisation coefficient is close to $K_{\max}$, we arrive at the conclusion that, in emulsions without supersensitisers, only one photoelectron out of the 100 formed ($f_1 = 0.99$) is used to form the latent image. The fact that in a number of instances the coefficient of supersensitisation by compositions exceeds the product of the coefficients for the individual substances may be associated with the change in the absorption of light by the dye under the influence of the supersensitisers. Thus phenomenological examination of the processes involving supersensitisation by mixtures of substances confirms the possibility of their acting in two consecutive stages of the self-desensitisation of dyes.

1. Supersensitisers of the first kind

We shall deal in greater detail with the effect of supersensitisers of the first kind, *i.e.* those adsorbable on AgHal. The adsorption of triarylphosphines on AgHal is undoubtedly associated with the ability of these compounds to form complexes with silver ions *via* the lone pair of $3s^2$ electrons on the phosphorus atom.¹⁰⁷ Thus the adsorption of phosphines in the presence of silver ions on the AgHal surface is apparently associated with the formation of a complex with these ions. On the other hand, in the presence of an excess of Hal^- ions on the AgHal surface, there is a possibility of either the desorption of these ions under the influence of the phosphines or of the adsorption of the phosphine with formation of a complex with the subsurface silver ions (another adsorption model).^{100, 109}

In the presence of an excess of halide ions, the surface of microcrystals in AgHal emulsions is known to be negatively charged and at a certain depth under the surface there is a region of a positive space charge generated by the interstitial silver ions.² There is a dynamic equilibrium between the surface silver ions and the subsurface interstitial ions. It may be that, when phosphines are introduced into the emulsion, the silver ions are 'drawn' from the region of the subsurface charge to the surface and complexes are formed with these ions.⁵

The interaction of triaryl derivatives of Group V elements having the general formula XAr_3 , where $\text{X} = \text{P}, \text{As}, \text{or Sb}$, with the surface of AgHal microcrystals has been investigated by IR spectroscopy and by measuring the ionic conductivity.¹¹⁰ According to IR and Raman spectra, vibrations ($\nu = 158 \text{ cm}^{-1}$) having the same frequency as the vibrations of the $\text{P} \rightarrow \text{Ag}^+$ bond in the complex $\text{AgBr} \cdot \text{PPh}_3$ are observed when PPh_3 is adsorbed on AgBr. Spectroscopic data led to the conclusion that the adsorption of the phosphine on AgBr results in the formation of a chemical bond between a surface Ag ion and the phosphorus atom of the PPh_3 molecule. This leads in its turn to a shift of the vibrational frequencies of the $\text{C}-\text{P}$ bond sensitive to the nature of the complex-forming agent. Similar changes in the IR spectra have been observed also for AsPh_3 and SbPh_3 . The compounds XAr_3 decrease the longitudinal ionic conductivity of sputtered AgBr layers, whereupon a definite relation is observed between the conductivity and stability constants of the silver complexes $\text{AgBr} \cdot \text{XAr}_3$.¹¹⁰ Measurements of the ionic conductivity of AgBr(I) emulsion layers by the dielectric loss method have shown that the adsorption of PPh_3 shifts the frequency maximum ($f_{\max}$) on the dielectric loss curve to lower frequencies. Since the conductivity of AgHal is proportional to $f_{\max}$ according to Sillars,¹¹¹ the observed shift of $f_{\max}$ indicates a decrease, following the addition of the phosphine, of the ionic conductivity generated by interstitial silver ions.

When silver complexes are formed on the surface of AgHal microcrystals, the surface charge changes. The interaction of the supersensitiser 4 with AgHal has been investigated by the luminescence method.¹⁰⁸ The adsorption of organic substances on

AgHal alters the surface charge, which influences in its turn the mechanism of the luminescence of paired iodine centres. Thus, if the surface charge of the AgBr(I) microcrystals is negative or the surface is uncharged, then, by irradiating an excited specimen with long-wavelength light at 77 K, it is possible to achieve a luminescence flash at the wavelength corresponding to the green luminescence band of the paired iodine centres. On the other hand, if the surface charge is positive by virtue of the excess of silver ions, a flash is not observed. It has been shown¹⁰⁰ that, when di-(*p*-anisyl)phenylphosphine 4 is introduced into a AgBr(I) emulsion prepared using poly(vinyl alcohol) as the binder, the green-band luminescence flash diminishes.

Additional evidence for the influence of the compounds XAr_3 on the surface charge of AgHal microcrystals has been obtained in experiments on a primitive coarse-grain AgBr(I) emulsion without chemical sensitisation.¹¹² In such emulsions, the subsurface sensitivity exceeds the surface sensitivity as a result of the positive space charge generated by the interstitial silver ions. The introduction of triphenylstibine into the emulsion leads to a sharp increase in the surface sensitivity owing to a redistribution of the surface charge, which is illustrated in Fig. 16. The subsurface sensitivity was determined after the successive etching of layers in a 1% $\text{Na}_2\text{S}_2\text{O}_3$ solution and on developing the specimens (after etching) in a glycine surface developer.

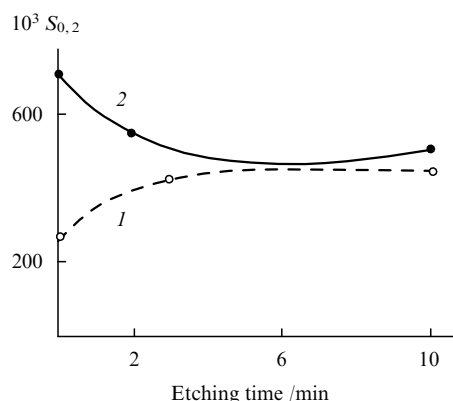


Figure 16. Dependence of the surface and subsurface sensitivity of light-sensitive layers based on a primitive AgBr(I) emulsion without additives (1) and containing triphenylstibine (2) on the etching time in 1% $\text{Na}_2\text{S}_2\text{O}_3$ solution. Triphenylstibine concentration 5×10^{-4} mol per mole of AgHal. Development — 8 min in a surface glycine developer.

The influence of adsorbed organic compounds on the surface charge has been considered in a number of studies. Thus the change in the sign of the AgHal photo-e.m.f. under the influence of gelatin has been explained¹¹³ by the redistribution of charges on the surface of microcrystals. It has been shown¹¹⁴ that, under certain conditions, the binding of the interstitial silver ions by the adsorbed gelatin leads to the appearance of a positive charge on the AgBr(I) surface. Tani¹¹⁵ explained the decrease in the bending of the electron bands of AgHal on the surface by the decrease in the subsurface positive charge under the influence of a series of stabilisers and antifogging substances — derivatives of tetraazaindenes and benzotriazole.

The appearance of a positive charge on the surface of AgHal microcrystals when triarylphosphines are adsorbed promotes the adsorption of infrachromatic dyes, which leads to an increase in the absorption and in the stability of the adsorbed dye, as happens with increase in the concentration of silver ions in the emulsion. This has been demonstrated in relation to the pentacarbocyanine 1 (cf. curves 2 and 4 in Fig. 12a). The stability of dye 1 in aqueous gelatin solutions and in the adsorbed state on the AgBr(I) emulsion at different pAg as well as the influence of di-(*p*-anisyl)phenylphosphine 4 on the stability of the adsorbed dye

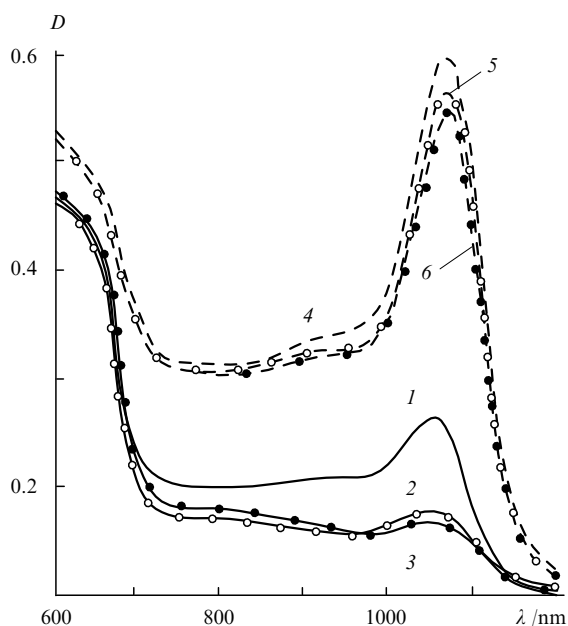


Figure 17. Absorption spectra of the pentacarbocyanine dye **1** in ultrafine-grain AgBr(I) emulsion at pAg 7.6 (1–3) and in the presence of supersensitiser **4** (4–6) as a function of the period during which the emulsion is allowed to stand at 40 °C: (1) and (4) after 5 min; (2) and (5) after 18 min; (3) and (6) after 30 min. Concentration of dye **1** 2.5×10^{-4} mol per mole of AgHal; concentration of supersensitiser **4** 1×10^{-2} mol per mole of AgHal.

have been investigated in detail.¹⁰³ Fig. 17 illustrates the increase in the absorption (cf. curves 1 and 4) and in the stability of the adsorbed dye **1** (cf. curves 1–3 and 4–6) under the influence of the phosphine **4**.

The observed bathochromic shift of the absorption of infrachromatic dyes under the influence of phosphines and the increase in the stability of the infrared dye can be accounted for by the formation of a ternary complex between the silver ions, the supersensitiser, and the dye $[\text{Ag}^+ \cdot \text{S} \cdot \text{Dy}]$.⁵

It has been shown¹¹⁰ that, when PAr_3 is adsorbed on AgBr, a new variable-composition organosilver bromide phase of the type $\text{AgBr} \cdot \text{PAr}_3$ may be formed in addition to the local chemical bond $\text{Ag}^+ - \text{P}$. Thus the dye may be adsorbed not on AgBr but on the organosilver bromide phase. In any case, both under conditions involving the participation of the ternary complex and on adsorption of the dye on the organosilver bromide phase, a spacer consisting of organosilver complexes is created between AgHal and the dye.

It is noteworthy that the action of phosphines differs from that of Riester's potentiators,^{87,88} which bind the surface silver ions *via* their mercapto-groups in the form of salts and thereby compensate their positive charge. Neutral (from the standpoint of the electrical charge) phosphines only partially compensate the charge of the silver ions in the complex, increasing the overall surface concentration of the silver ions and hence promoting the adsorption of the dye and the interaction of the photoexcited infrared dye with silver ions. The spacer should not prevent electron transfer from Dy^* *via* the silver ions to AgHal, but it may inhibit significantly the secondary reactions involving the oxidation of the generated silver atoms by dye molecules in the ground state. Indeed, in the presence of di-(*p*-anisyl)phenylphosphine, the desensitisation of silver halides by infrared dyes diminishes.¹⁰² Such insulation of the strongly fogging infrared dyes from AgHal leads to a sharp diminution in the fogging of infrared emulsions in the presence of triarylphosphine.

It may be expected that the effect of uncharged complex-forming agents examined above is definitely associated with the

complex-forming capacity of the silver ions. To test this hypothesis, a study was made of a series of triphenyl derivatives having the general formula XPh_3 , where X = N, P, As, Sb, or Bi. The photographic effect of this series of compounds had not been investigated previously on coarse-grain AgBr(I) emulsions sensitised by tricarbo-cyanine.¹¹⁶ It has been shown that the maximum supersensitisation effect is attained in the case of triphenylphosphine, which is followed by triphenylarsine and triphenylstibine; triphenylamine and triphenylbismuthine hardly influence the photographic properties of emulsions.

The effect of compounds of the above series has been investigated on an ultrafine-grain AgBr(I) emulsion ($d = 0.05 \mu\text{m}$) sensitised by the pentacarbocyanine **1**.¹⁰⁹ The introduction of these compounds as well as di-(*p*-anisyl)phenylphosphine **4** leads to an increase in the absorption by the adsorbed dye. In terms of their effect, the test compounds can be arranged in the sequence $\text{N} < \text{Bi} < \text{P} < \text{As} \approx \text{Sb}$. The absorption curves for the emulsions are presented in Fig. 18. In conformity with the data of Akhmedzyanov *et al.*,¹¹⁶ it was established that NPh_3 and BiPh_3 do not have a positive photographic effect, whereas PPh_3 , AsPh_3 , and SbPh_3 induce an increase in the spectral sensitivity in the long-wavelength band. At pAg 8.6, the supersensitisation coefficients for compounds in the series PPh_3 , AsPh_3 , and SbPh_3 are 2.1, 2.9, and 5.8 respectively.

In order to estimate the complex-forming capacities of the

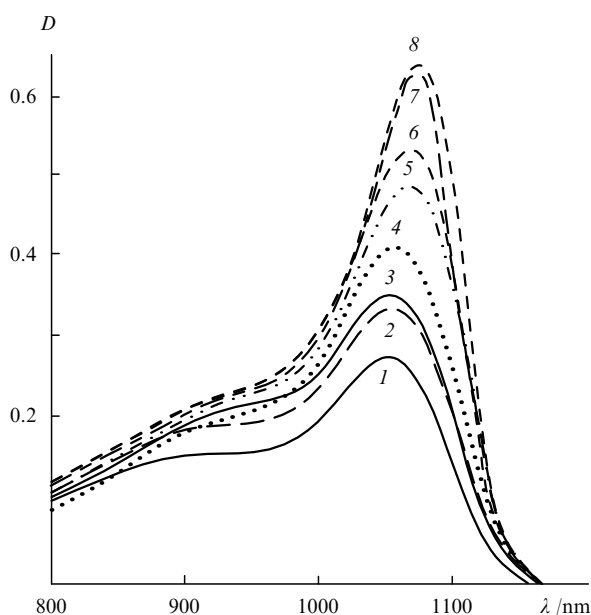


Figure 18. Absorption spectra of ultrafine-grain AgBr(I) emulsion sensitised by dye **1** at pAg 7.6: (1) without additives; (2) NPh_3 ; (3) additional amount of AgNO_3 ; (4) BiPh_3 ; (5) PPh_3 ; (6) $\text{P}(\text{CH}_3\text{OC}_6\text{H}_4)_2\text{Ph}$; (7) SbPh_3 ; (8) AsPh_3 . Concentration of dye **1** 3×10^{-4} mol per mole of AgHal; concentration of additives 1×10^{-2} mol per mole of AgHal.

compounds, the changes in the pAg of the emulsions were measured after the introduction into the latter of equal molecular amounts of the above substances (10^{-2} mol per mole of AgHal). The initial pAg 7.6 changed to 7.8, 7.8, 8.5, 8.6 and 8.65 after the addition of NPh_3 , BiPh_3 , PPh_3 , AsPh_3 , and SbPh_3 respectively, while the initial pAg 6.6 changed to 6.95, 6.95, 7.9, 7.9, and 8.2. Thus the absence of a photographic effect by NPh_3 and BiPh_3 is associated with their weak complex-forming capacity. The compounds AsPh_3 and SbPh_3 have approximately the same complex-forming capacities in relation to silver ions in solution, but PPh_3 is a stronger complex-forming agent.¹¹⁷ The observed increase in the supersensitising activity in the series $\text{PPh}_3 < \text{AsPh}_3 < \text{SbPh}_3$ is apparently associated with the different adsorbabilities of these

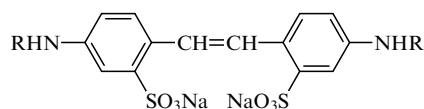
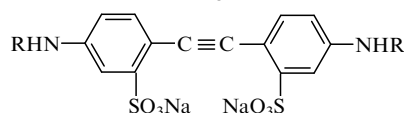
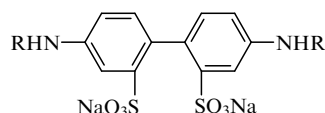
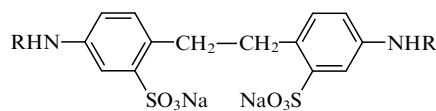
compounds on AgHal, which are determined by the molecular geometry. Hence it follows that these two properties must be considered jointly.

The specificity of the action of the compounds XPh_3 ($X = N, P, As, Sb$) as well as $(PhC \equiv C)_n PPh_3 - n$ has been attributed¹¹⁰ to the structure of the surface organosilver bromide complexes. The structure of the complex formed — the stoichiometric composition, the phase state, the type of crystal lattice, and the structure of the electron bands — should determine the effectiveness of the interaction with it of the spectral sensitiser in the ground and photoexcited states. For example, when PPh_3 is adsorbed on a AgBr emulsion with cubic microcrystals at pAg 7.5 and on a coarse-grain AgBr(I) emulsion with cubooctahedral microcrystals at pAg 8.5, two different surface complexes, differing in their IR spectra, are formed. The vibrational frequencies of the ν -modes in these spectra are close to those of the bond vibrations in the complexes $Ag_2Br_2 \cdot PPh_3$ and $AgBr \cdot PPh_3$ (1099 and 1095 cm^{-1} respectively). On spectral sensitisation at the wavelength corresponding to the absorption band of the infrared dye, a decrease in the intensity of the band with $\nu = 1099\text{ cm}^{-1}$ is observed, while the band with $\nu = 1095\text{ cm}^{-1}$ changes little under these conditions.¹¹⁸ This indicates different photochemical reactivities of the surface complexes.

A similar picture has been observed for supersensitiser **4**. On the basis of Ahrlund's data,¹¹⁷ it was concluded that organosilver complexes may participate in the primary step of the spectral sensitisation by the infrared dye, undergoing photochemical decomposition with formation of a silver atom. Furthermore, the photographic activity of the complexes is manifested in secondary dark stages as a result of the inhibition of the recombination and oxidation reactions of silver atoms.

We shall now consider the activity of another supersensitiser of practical importance — the disodium salt of bistriazinylaminostilbene-*o,o'*-disulfonic acid **6**. The increase in the adsorbability of dyes under the influence of supersensitiser **6** has been demonstrated^{99, 100} and is illustrated in Fig. 19, which presents the isotherms for the adsorption of penta- and tetra-carbocyanines on AgBr powder without a supersensitiser and in the presence of

compound **6**. The interaction of a series of derivatives of aromatic diamino-compounds having the general formula $RHN-Ar-NHR$ with cyanine dyes in solutions and on the AgHal surface has been investigated in detail.^{119, 120} In order to establish the nature of the interaction of the supersensitisers and spectral sensitisers in adsorption on AgHal, the principal types of interaction were examined in the above studies stage by stage: (1) dye — supersensitiser, (2) supersensitiser — substrate, and (3) dye — supersensitiser — substrate. The following supersensitisers were investigated:

**8****9****10****11**

The peripheral groups R were 1,3,5-triazinyl and acyl substituents. The studies were carried out on quino-4,4'-cyanines with different lengths of the polymethine chain and also on thiapoly-carbocyanine dyes.¹²¹

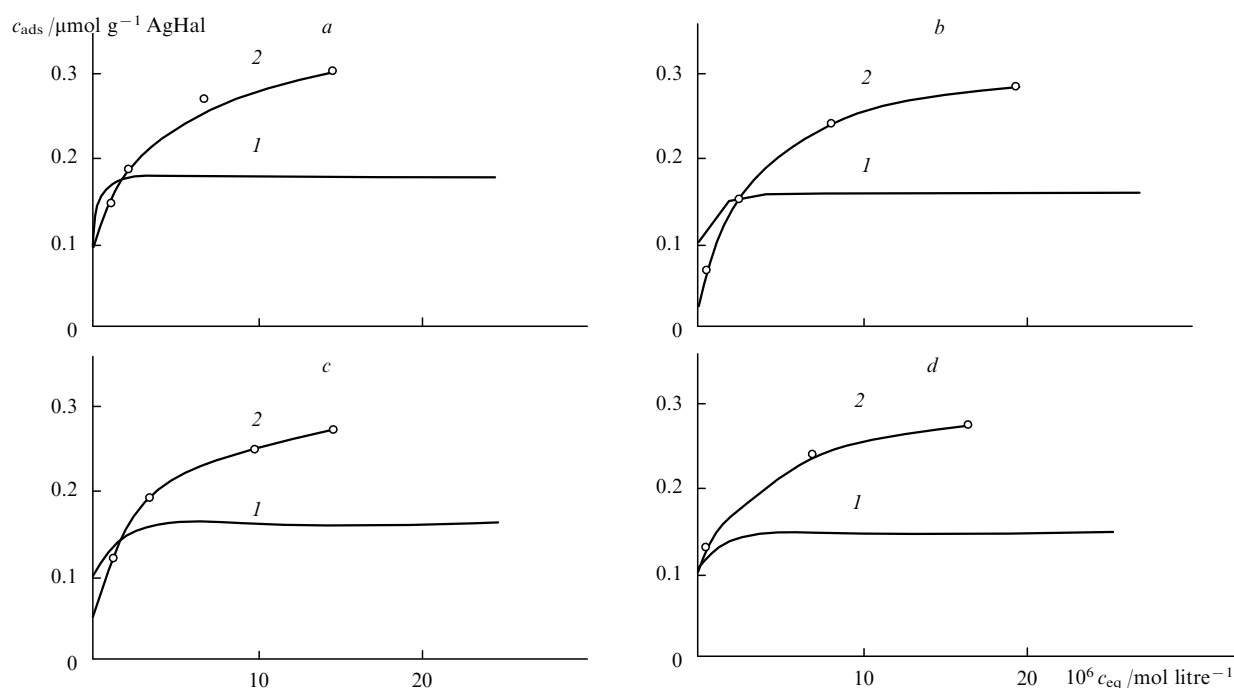


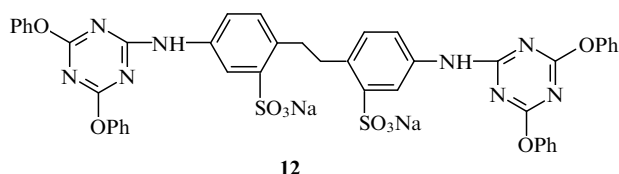
Figure 19. Isotherms for the adsorption of penta- and tetra-carbocyanines on a AgBr preparation from alcoholic solutions (*1*) and after preliminary adsorption of supersensitiser **6** (*2*) at 25 °C; dye: (a) 3,3'-diethylthiatetracarboyanine iodide; (b) 3,3'-diethyl-9,11-(β,β -dimethyltrimethylene)thiatetracarboyanine iodide; (c) 3,3'-diethylthiapentacarboyanine iodide; (d) 3,3'-diethyl-9,11,9',11'-bis(β,β -dimethyltri-methylene)thiapenta-carboyanine iodide; c_{ads} = amount of adsorbed dye; c_{eq} = equilibrium concentration of dye.

It has been shown¹²⁰ that in solutions the interaction in the dye–supersensitiser system is in the nature of the π – π interaction of the two planar systems of the dye and the supersensitiser. A condition for the effective interaction of the π -system of the dye with the π -system of the compound RHN–Ar–NHR is both the presence in the supersensitiser structure of a central π -conjugated Ar skeleton and of auxochromic fragments R capable of π -conjugation with the central skeleton *via* the nitrogen atoms of the amino-groups. A bathochromic shift of the stretching vibrations of the NH groups and also a change in the profile of the absorption bands due to the SO₃[–] groups¹²⁰ were observed in the IR spectra of supersensitisers adsorbed on AgBr microcrystals. This led to the conclusion that the nature of the adsorption centres is the same: NH and SO₃[–] groups. The IR spectra of *p,p'*-bis(4,6-diaminophenyl-1,3,5-triazin-2-yl-amino)stilbene-*o,o'*-disulfonic acid **6a**, adsorbed on AgBr microcrystals had been obtained earlier¹²² in the frequency range 700–1700 cm^{–1}.

It was concluded that the test compounds do not form a strong chemical bond with the silver ions. This conclusion was confined by the small influence of supersensitisers of the above type on the ionic conductivity of sputtered AgBr layers.¹²⁰

It has been concluded¹²⁰ that the SO₃[–] and NH groups participate in the interaction of compounds **8–11** with AgHal, the main π -system of the molecules being hardly involved. The interaction *via* the SO₃[–] groups should be most probably regarded as the substitution of halide ions on the AgHal surface by ArSO₃[–] ions and not as the binding of interstitial or surface silver ions by analogy with the adsorption of compounds of the type of triarylphosphines. One may imagine that, in the adsorption of compound **6**, and similar derivatives, the molecule assumes an orientation such that its aromatic component is separated from AgHal by SO₃[–] groups. In the case of compound **6**, the planar π -conjugated part of the molecule is arranged parallel to the AgHal surface and is at a definite distance from the latter. Conventionally this constitutes the ‘table on two SO₃[–] legs’ model. The NH groups can also serve as ‘supports’. It is noteworthy that this model resembles the Riester potentiators model.^{87, 88}

The observation of the interaction of the nonplanar supersensitiser **12** with the dye on the AgHal surface should be regarded as the most important result of the above study.¹²⁰

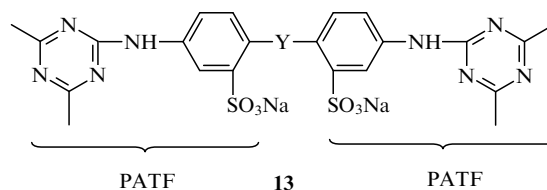


12

Like supersensitisers with π -conjugated aromatic fragments Ar, compound **12** induced a bathochromic shift of the absorption maximum of the adsorbed infrared dyes, an increase in the absorption intensity, and a supersensitisation effect comparable other in magnitude to that of compound **6**. On the other hand, it has been found that compound **12** does not interact with the dye in solution.

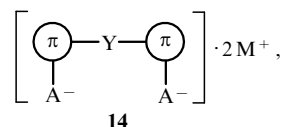
In order to account for the photographic activity of this sensitiser and the bathochromic shift of the absorption maximum of the dye, it is necessary to postulate a flattening of the molecule of compound **12** following adsorption on AgHal. Consequently, the situation on AgHal changes significantly compared with that in solution, *i.e.* the π – π interaction between the supersensitiser and the dye becomes possible in the dye–supersensitiser–AgHal ternary system. In this case, a decisive factor for the dye–supersensitiser interaction may be not only (and perhaps not so much) the planarity of the entire molecule of compound **12** but also the geometrical correspondence between certain parts of the two interacting systems. Such a part in the molecule of compound **12** may be the phenylaminotriazinyl fragment (PATF), which interacts with AgHal *via* the SO₃[–] and NH groups according to IR spectra.¹²⁰

It has been postulated¹²⁰ that, in more general terms, a molecule having the following structure should be photographically active:



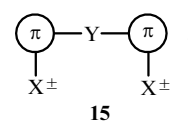
Y = –(CH=CH)_n–, –(C≡C)_n–, –(CH₂–CH₂)_n–, where n = 1, 2, 3.

in which the two phenylaminotriazinyl fragments are disposed at a certain distance specified by the bridging group Y. This distance between the two π -systems is apparently in fact the principal factor determining the photographic activity of the supersensitisers. The geometrical requirements which must be met by the supersensitiser may be determined both by the AgHal lattice constant and by the structure of the supersensitising dye. It is probably quite unnecessary that PATF should be the anionic π -fragment. Other compounds can also assume the role of such π -fragments.⁵ In a general form, the structure of the supersensitiser can be represented as follows:



where A[–] is the acid group, π the conjugated system, Y the bridging group, and M⁺ the cation. Thus one is dealing with bisanionic structures of supersensitisers consisting of two π -systems with negative charges localised on the acid groups and linked to one another *via* the bridging Y group.

A certain analogy between the supersensitisers of the class under consideration and the bridged bisquaternary salts of heterocyclic bases used for the supersensitisation of orthochromatic and panchromatic dyes, as a rule in the *J*-aggregated state, is striking.^{123–125} Therefore, continuing the generalisation, one may put forward the hypothesis that there is a single principle underlying the supersensitising activity of bridged compounds containing at least two cationic or anionic fragments:



where X[±] is a group with a localised positive or negative charge. The specificity of the activity of particular supersensitisers having structure **15** may be associated with the following structural features of the dyes: (1) the overall charge on the spectral sensitiser (cationic, betaine, anionic), (2) the distribution of the π -charge density in the molecule, (3) the polarisability of the molecule, (4) the electron-donating or electron-accepting capacity of the π -system, *etc.*¹²⁰ Since infrared dyes are as a rule used in the form of cations, the suitability of the bisanionic compounds **14** as supersensitisers may be associated with purely electrostatic factors.

The question naturally arises what is the mechanism of the supersensitising activity of the test compounds. The photographic activity of compounds of the given class can apparently be usefully considered within the framework of the insulation model, according to which the supersensitiser creates a ‘spacer’ of molecular dimensions between the dye and AgHal.^{5, 6} This is illustrated conventionally in Fig. 20. The insulation model is in essence similar to Riester’s model,⁸⁸ but there are also significant differences associated with the mechanism of the interaction in the dye–supersensitiser–AgHal system. The insulating spacer prob-

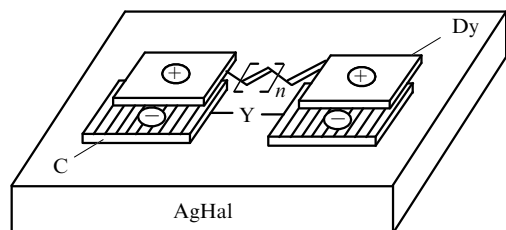
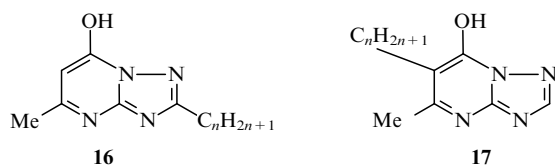


Figure 20. A model of the adsorption of a supersensitizer and dye on AgHal.

ably does not prevent electron transfer from the excited Dy^* molecule to AgHal (apparently *via* a tunnelling mechanism), but it does prevent the reverse capture of photoelectrons by the dye radical-cations formed or by neighbouring electron-accepting Dy molecules in the ground state in accordance with Scheme 1.

The activity of the supersensitizer 2-heptyl-4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene **5**, which induces an increase in the absorption by the dye adsorbed on AgHal (Fig. 13, Table 1), is caused not only by the presence of the tetraazaindene ring but also to a large extent by the presence of the long (C_7H_{15}) alkyl group. It has been shown^{94, 126} that the supersensitising activity of alkyl derivatives of tetraazaindene and 1,2,4-triazole increases with increase in the length of the alkyl group from C_1 to C_7 , *i.e.* with increase in the hydrophobicity of the compounds. The supersensitising activity of 2-alkyl (compound **16**) and 5-alkyl (compound **17**) derivatives of tetraazaindene on emulsions sensitised by thiapenta- and thiatetra-carbocyanines **1** and **2** has been investigated.¹²⁷



$n = 1-11$.

In the series of compounds investigated, the hydrophobicity increased steadily on passing from C_1 to C_{11} alkyl substituents. The 2-alkyl derivatives **16** showed the greatest photographic activity, especially on emulsions sensitised by the pentacarbocyanine **1**. The results obtained are presented in Fig. 21. The supersensitisation effect increases the spectral sensitivity by a factor of 11. It is striking that an abrupt jump in the effectiveness of the sensitisation is observed on passing from $n = 4$ to $n = 6$. On further increase in the length of alkyl group from $n = 6$ to $n = 11$, the effectiveness changes little.

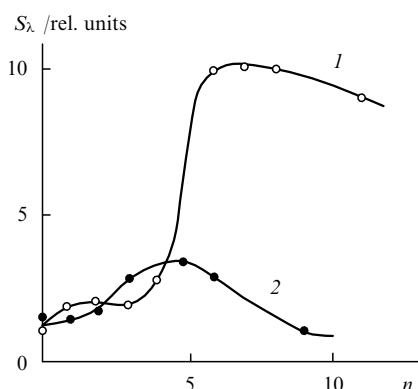
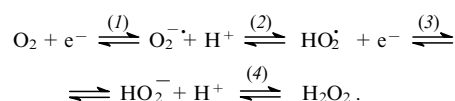


Figure 21. Dependence of the spectral sensitivity of photographic emulsions sensitised by the thiapentacarbocyanine **1** on the number of carbon atoms in the alkyl groups of compound **16** (1) and **17** (2).

The effectiveness of 5-alkylated derivatives **17** is appreciably smaller than that of compound **16** (cf. curves 2 and 1 in Fig. 21). The increase in the spectral sensitivity of emulsions with the tetracarbocyanine **2** is smaller than for emulsions with the pentacarbocyanine **1**, but the nature of the activity of the supersensitisers remains the same.¹²⁷ The supersensitisation by compounds **16** and **17** can be partly due to the increase in the adsorbability of the supersensitisers with increase in the length of the alkyl substituent, which has been observed, for example, for a series of *N*-alkyl derivatives of cations.² Comparison of the results obtained for 2- and 5-alkyl derivatives of tetraazaindene permits the conclusion that the photographic activity of supersensitisers is determined not only by their hydrophobicity but also by the disposition of the hydrophobic groups in the molecule. It is also possible that the higher photographic activity of the 2-alkyl derivative **16** is associated with the location of the alkyl substituents at the photographically active fragment of the molecule.¹²⁷

The mechanism of the action of supersensitisers of the first kind, *i.e.* those absorbable on AgHal, has been investigated in model electrochemical experiments. The inhibition of electron transfer to oxygen and protons by supersensitisers has been demonstrated extremely clearly in experiments designed to investigate the influence of these compounds on the polarographic oxygen reduction waves in aqueous alcoholic media.¹²⁸ In this case, the mercury dropping electrode and not photoexcited silver halide served as the source of electrons for oxygen. Under the usual conditions, in aqueous media, oxygen is reduced at the mercury electrode to hydrogen peroxide in accordance with Scheme 2.¹²⁹

Scheme 2



Under these conditions, the reversibility of stages 1–3 depends on the pH of the medium. It was shown that the introduction of di-(*p*-anisyl)phenylphosphine **4** into the solution shifts the half-wave oxygen reduction potential towards more negative values and diminishes the height of the wave (cf. curves 1 and 3 in Fig. 22). The shift of the wave is caused by the inhibition of electron transfer in stage 1 (Scheme 2) owing to the formation on the electrode of an insulating film preventing electron transfer to oxygen. Calculation of the electron transfer rate constant showed that, in the presence of the phosphine **4**, the rate of transfer diminishes by a factor of 3000. Compound **5** induces a smaller effect. In its presence, the rate falls by a factor of 400 (cf. curves 2 and 3 in Fig. 22).

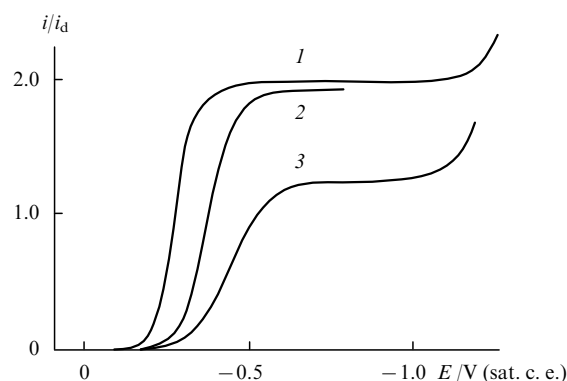


Figure 22. Polarographic curves for the reduction of oxygen in an air-saturated aqueous propanol solution at pH 13.0: (1) without supersensitizer; (2) with supersensitizer **5**; (3) with supersensitizer **4**. Concentration of supersensitisers 6.2×10^{-4} mol per mole of AgHal.

The decrease in wave height in the presence of the phosphine **4** down to virtually the one-electron value is associated with the inhibition of stage 2 by the insulating film. Oxygen is then reduced to O_2^- and not to hydrogen peroxide. The effect of the phosphine **5** is smaller in this stage than that of the phosphine **4**. In terms of their inhibiting effect on electron transfer and the inhibition of the protonation of O_2^- , the supersensitisers XPh_3 ($X = P, As, Sb$) may be arranged in the sequence¹²⁸ $SbPh_3 > AsPh_3 > PPh_3$. The average ratio of the pore area in a film comprising the compounds XPh_3 on the electrode to the area occupied by one molecule is 0.30, 0.32, and 0.42 for $SbPh_3$, $AsPh_3$, and PPh_3 respectively, *i.e.* the density of the insulating film diminishes in the sequence $SbPh_3 > AsPh_3 > PPh_3$. Thus the functions of certain supersensitisers of the first kind involve not only the creation of an 'insulating spacer' but also the formation of a hydrophobic spacer inhibiting secondary processes involving water protons.

2. Supersensitisers of the second kind

We shall now proceed to the consideration of supersensitisers of the second kind, *i.e.* compounds which are poorly adsorbable on AgHal and the activity of which is apparently associated mainly with their hydrophobic nature. The secondary oxidation reactions with participation of oxygen and water in stages 2–4 and 7 (Scheme 1) are in fact inhibited precisely because of the hydrophobic nature of the supersensitisers. The activity of *C,N*-diphenylnitrone **7**, which supersensitises infrared light-sensitive layers both individually and in compositions with supersensitisers of the first kind, has already been considered above. The supersensitising effect of nitrones was discovered in 1975 at the State Research and Design Institute of the Chemical-Photographic Industry (GOS-*NIKhIMFOTOProekt*). *C,N*-Diphenylnitrone is weakly adsorbed on AgBr.⁹⁹ According to IR spectroscopic data (in the frequency range 400–4000 cm^{-1}), no changes are observed in the vibrational spectrum of the nitrone **7** after its adsorption on AgBr.⁷⁶ The weak interaction of nitrones with AgHal is also indicated by their small influence on the ionic conductivity of AgBr emulsions.⁷⁶

In order to test experimentally whether organic hydrophobic compounds do really inhibit reactions involving electron loss by silver halide, a study was made of the influence of a series of substances (*C,N*-diphenylnitrone, azobenzene, azoxybenzene) on the luminescence of spectrally sensitised AgBr microcrystals.¹³⁰ If such compounds are able to insulate the surface of the emulsion microcrystals from interaction with oxygen and water, then one may expect an increase in the concentration of electrons in the conduction band and on the surface capture levels and hence an increase in the intensity of the low-temperature luminescence of microcrystals and dyes, arising on recombination of electrons with the holes of AgHal and the dyes respectively.

Measurements of the low-temperature (77 K) luminescence of a fine-grain AgBr emulsion have been carried out with excitation by light corresponding to the region of the intrinsic absorption by AgBr ($\lambda = 365$ nm). Fig. 23*a* presents the luminescence spectra of the emulsion before and after the introduction of solutions of the nitrone **7**. It follows from the results presented in the figure that the nitrone **7** increases the intensity of the orange luminescence of the AgBr microcrystals. Furthermore, the intensity of the optical luminescence flash, stimulated by infrared light, increases. Similar results have been obtained for azobenzene and azoxybenzene.

It is striking that the increment in the luminescence intensity under the influence of the supersensitisers investigated corresponds to an increase in the photographic activity of the compounds. Thus the facts described agree with the hypothesis that hydrophobic substances on the surface of emulsion microcrystals prevent the liberation of photoelectrons into the medium and hence increase the intensity of the recombination luminescence and the light sum localised in deep traps.

The fluorescence and phosphorescence bands of the dyes are observed in the luminescence spectra of silver bromide emulsions sensitised by thiacyanines and thiadicyanines: with

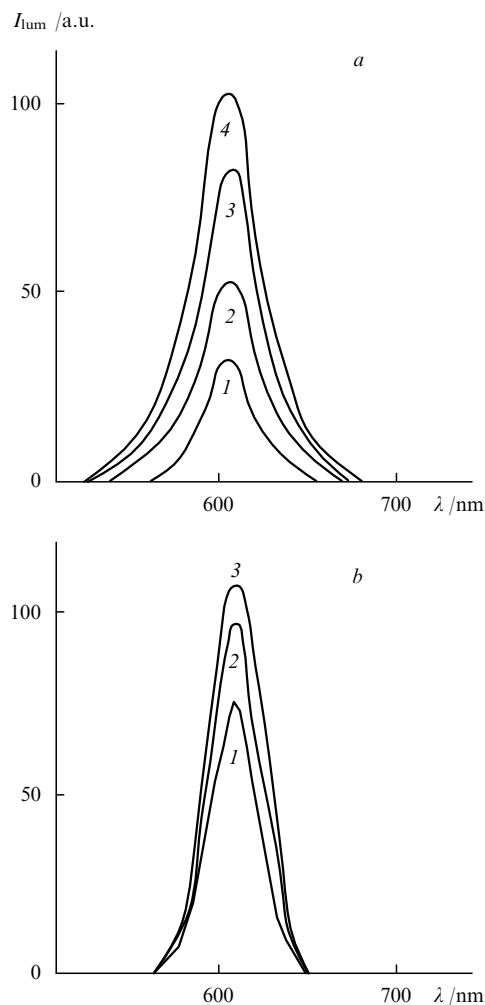
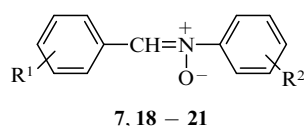


Figure 23. Luminescence spectra of a AgBr emulsion: (a) before (1) and after (2–4) introduction of compound **7** at different concentrations (10^{-3} mol per mole of AgHal) (2) 1; (3) 5; (4) 10; (b) before (1) and after the introduction of azobenzene (2) and azoxybenzene (3) at a concentration of 10^{-3} mol per mole of AgHal.

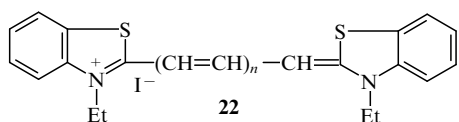
$\lambda_{max} = 615$ and 740 nm in the former case and with $\lambda_{max} = 770$ and 900 nm in the latter. The luminescence appears as a result of the recombination of free electrons with holes localised by dye molecules. As was to be expected, the addition of the nitrone **7** to spectrally sensitised emulsions leads to an increase in the intensity of the low-temperature recombination luminescence, which is due to a sharp decrease in the probability of the capture of photoelectrons by molecular oxygen and moisture.¹³⁰

Akhmerov *et al.*¹³¹ investigated in detail by luminescence and photographic methods the activity of nitrones having the general formula



$R^1 = H, R^2 = H$ (**7**); $R^1 = o\text{-Cl}, R^2 = H$ (**18**); $R^1 = H, R^2 = p\text{-Me}$ (**19**); $R^1 = p\text{-OMe}, R^2 = p\text{-Me}$ (**20**); $R^1 = o\text{-Cl}, R^2 = p\text{-Me}$ (**21**).

The studies were performed on a fine-grain AgBr emulsion spectrally sensitised by thiapolycyanines **22** with different lengths (n) of the polymethine chain.



The activity of the nitrones was compared with their hydrophobicity estimated from the partition coefficients (K_{part}) of the substances in the 1-octanol–water two-phase system.¹²⁷ A correlation between the hydrophobicity of the nitrones and their ability to increase the intensity of the low-temperature luminescence of AgBr and the dyes was demonstrated. Fig. 24 presents the dependence of the intensity (μ_1) of the orange luminescence of AgBr on the hydrophobicity of the nitrones. The luminescence intensity increases with increase in hydrophobicity. Fig. 25 illustrates the dependence of the effectiveness of the activity of nitrones on the length of the polymethine chain of the thiapolycarbocya-

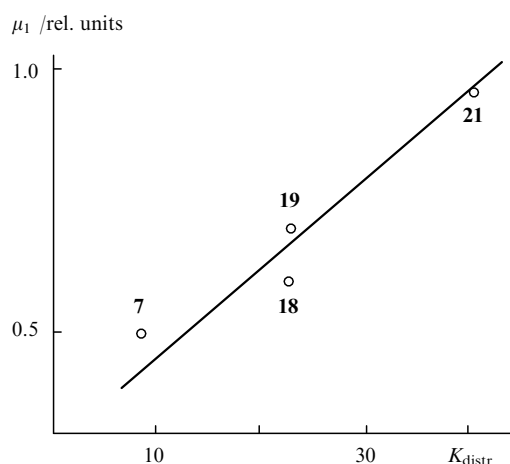


Figure 24. Dependence of the intensity of the orange luminescence of a AgBr emulsion on the hydrophobicity of the nitrones **7**, **18**, **19**, and **21**. Concentration of nitrones — 3×10^{-3} mol per mole of AgHal. $\mu_1 = (I - I_0)/I_0$ (I_0 and I are the intensities of the AgBr luminescence in the absence and presence of the nitrone respectively).

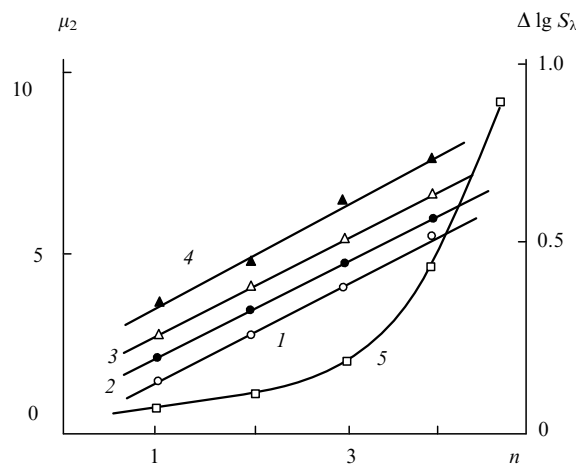


Figure 25. Dependence of the intensity of the luminescence of dyes (**1**–**4**) and of the increase in spectral sensitivity (**5**) for a AgBr emulsion sensitised by thiapolycarbocyanines **22** after the introduction of the nitrones **18**–**21** [(**1**) **18**; (**2**) **19**; (**3**) **20**; (**4**) **21**] on the length (n) of the polymethine chain of the dyes. Concentration of dyes — 5×10^{-5} mol per mole of AgHal; concentration of nitrones — 3×10^{-3} mol per mole of AgHal. $\mu_2 = (I - I_0)/I_0$ (I_0 and I are the intensities of the fluorescence of the dyes at the maximum in the absence and presence of a nitrone respectively); $\Delta \lg S_\lambda = \lg(S_\lambda/S_\lambda^0)$ (S_λ^0 and S_λ are the spectral sensitivities in the absence and presence of a nitrone respectively).

nines **22**. For all the nitrones, an increase in the intensity of the luminescence of the dyes (μ_2) with increase in chain length is observed, the effectiveness of the nitrones being greater the greater their hydrophobicity (cf. curves **1**–**4** in Fig. 25). The figure also illustrates the effect of the supersensitisation ($\Delta \lg S_\lambda$) of the light-sensitive layers with thiapolycarbocyanines by the nitrone **21** (curve **5** in Fig. 25). The results can be accounted for within the framework of Scheme 1 by the self-desensitisation of the dyes. Indeed, with increase in the length of the polymethine chain of the dyes, their vacant level under the AgBr conduction band becomes deeper and hence there is an increase in the probability of electron capture in stage **1** of Scheme 1. The effectiveness of the insulating spacer, which prevents electron transfer from $\text{Dy}^{\cdot-}$ to oxygen and the water protons, should therefore increase with increase in the length of the polymethine chain, which agrees with experimental results. The increase in effectiveness with increasing hydrophobicity of the compounds can also be explained within the framework of the supersensitisation scheme examined above.

The hydrophobic properties of nitrones are manifested by a shift of the polarographic half-wave reduction potential of oxygen and also by a decrease in wave height (Fig. 26).¹²⁸ The increase in the hydrophobicity of the nitrones, associated with the introduction of chlorine atoms into the benzene ring, is accompanied by the inhibition of electron transfer to the oxygen and the protonation of $\text{O}_2^{\cdot-}$. In terms of its influence on the inhibition of the electron transfer from the electrode to the oxygen, the nitrone **21** is close to di-(*p*-anisyl)phenylphosphine **4**, while in terms of the inhibition of the protonation of $\text{O}_2^{\cdot-}$ it is 2.5 times more effective than the latter.¹²⁸

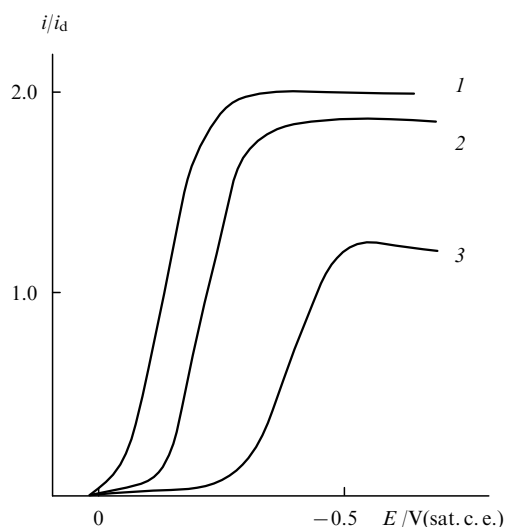


Figure 26. Polarographic curves for the reduction of oxygen in an air-saturated 10% aqueous propanol solution at pH 11.0; (**1**) without supersensitiser; (**2**) with the nitrone **7**; (**3**) with the nitrone **21**. Concentration of supersensitisers — 6.2×10^{-4} mol per mole of AgHal.

According to Scheme 1, the probability of the dye self-desensitisation processes increases with increase in the concentration of the electron-accepting dye and in its electron affinity. The effectiveness of the supersensitisation by nitrones inhibiting the loss of photoelectrons should therefore also increase with increasing concentration of the dye and of its affinity. Fig. 27 presents the dependence of the supersensitisation coefficients (K_s) on the dye concentration for photographic emulsion6 sensitised by the thiapentacarbocyanine **1** and containing the supersensitiser **4** of the first kind and its compositions with supersensitisers of the second kind — the nitrones **7** and **21**.⁷⁶ According to Fig. 27, with increase in the concentration of the dye **1** the supersensitisation effect produced by the phosphine **4** diminishes (straight line **1**),

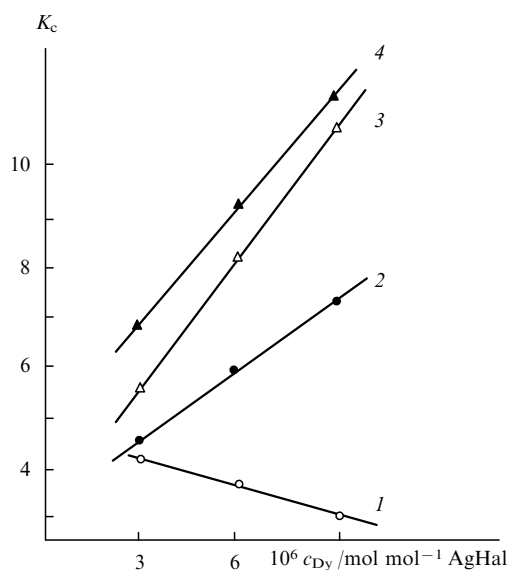
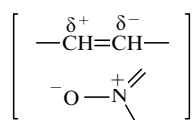


Figure 27. Dependence of the coefficient of the supersensitisation of photographic emulsions sensitised by the thiapentacarbocyanine **1** and containing supersensitisers **4** (1), **4** + **7** (2, 3), and **4** + **21** (4) on the dye concentration. Concentrations of supersensitisers (mol per mole of AgHal): 9×10^{-4} of compound **4**, 5×10^{-3} (2) and 1×10^{-2} (3) of compound **7**, and 2.5×10^{-3} of compound **21**.

while that by the additionally introduced nitrone **7** (or **21**) actually increases (straight lines 2–4). This clearly demonstrates the difference between the mechanisms of the supersensitisation by the two types of substances.

The photographic activity of nitrones has been attributed¹³² to a certain combination in its molecule of the hydrophobic aryl rings and the polar oxyazamethine group. Calculations showed¹³³ that the length of the N–O bond (1.406 Å) is close to that of the C–C bond in the polymethine chain of cyanines; this makes possible quadrupole interactions of the type



with the alternating charges of the chain. As a result of such interaction, part of the polymethine chain of the dye may be insulated by the nitrone from oxygen and water.

The acceleration of the regression of the latent image centres by the molecules of infrared dyes in the ground state in conformity with Scheme 1 (Fig. 10) was already examined above. It is essential to emphasise that stable latent image centres (LIC), consisting of at least four (or more) silver atoms and formed in the course of the exposure of the light-sensitive layers, are oxidised in model investigations whereas in a real spectral sensitisation process mainly silver atoms with a low stability (precentres of the latent image) are oxidised in the course of the desensitisation. Nevertheless, model studies are useful for discovering the general rules governing the oxidation of silver particles.

The influence of supersensitisers on the regression of LIC has been investigated on a monodisperse AgBr(I) emulsion with sulfur sensitisation.^{76, 132} The activity of supersensitisers of the first kind (compounds **4** and **6**) and second kind (compound **7**) and of their compositions has been investigated. Fig. 28 presents curves for the regression of LIC, characterising the variation of the intrinsic (S_i) and spectral (S_λ) sensitivity of photographic emulsions at 35 °C and 100% humidity. According to the results, the phosphine **4** retards somewhat the decrease in S_i and S_λ for the light-sensitive layers (curves 1 and 2 in Figs 28a and 28b). A similar

picture is observed in the presence of supersensitiser **6** (cf. curves 1 and 3). It is striking that the hydrophobic compound (the nitrone **7**) inhibits the regression of LIC to a greater extent than compounds **4** and **6**. Special mention should be made of the considerable decrease in the degree of regression (by a factor of 7–10) in the presence of a composition comprising supersensitisers of the first kind (compound **4**) and second kind (compound **7**) (cf. curves 1–4 and 5 in Figs 28a and 28b). Thus model studies on the regression of LIC agree with the hypothesis that oxidation reactions involving dyes in the ground state are inhibited by supersensitisers of the first and second kind.

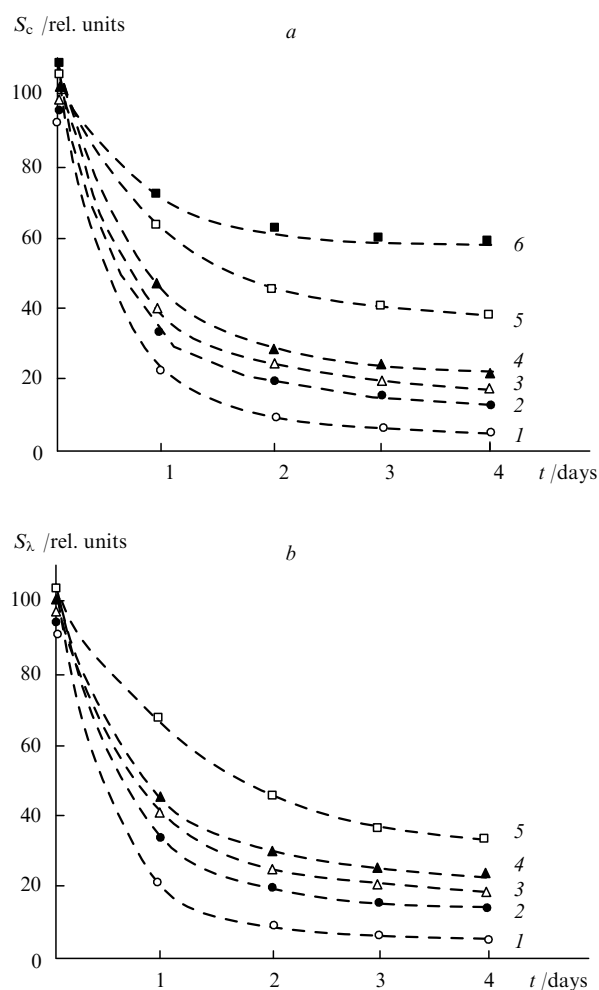


Figure 28. Variation of the intrinsic (S_i) (a) and spectral (S_λ) (b) sensitivities of photographic emulsions sensitised by the thiapentacarbocyanine **1** individually and in the presence of supersensitisers at 35 °C and 100% humidity: (1) dye **1**; (2) **4** + **1**; (3) **6** + **1**; (4) **1** + **7**; (5) **4** + **1** + **7**; (6) without a dye. Dye concentration 18×10^{-6} mol per mole of AgHal; concentrations of supersensitisers (mol per mole of AgHal): 3×10^{-4} of compound **4**, 5×10^{-3} of compound **6**, and 1×10^{-2} of compound **7**.

The method involving the evacuation of photographic emulsions before exposure¹³⁴ has been used⁷⁶ to obtain additional experimental proof of the role of oxygen and moisture in dye self-desensitisation processes and also of the inhibiting influence of supersensitisers on these secondary processes. As was to be expected, on exposure *in vacuo* of a photographic emulsion sensitised by the thiapentacarbocyanine **1**, the spectral sensitivity of the emulsion increased by a factor of 2.7 (Table 3), while after the admission of air it fell again and virtually reached the initial value.

A supersensitiser of the first kind (compound **4**) increased the spectral sensitivity of an emulsion of this type by a factor of 4. On

Table 3. The influence of evacuation on the photographic sensitivity of infrared emulsions (pAg 7.6).

Exposure conditions	$S_\lambda(1)$	$D_0(1)$	$S_\lambda(4+1)$	$D_0(4+1)$	$S_\lambda(1+7)$	$D_0(1+7)$	$S_\lambda(4+1+7)$	$D_0(4+1+7)$
Before evacuation	1.0	0.35	4.0	0.25	5.0	0.48	11.0	0.35
<i>In vacuo</i>	2.7	0.25	6.0	0.30	7.5	0.60	11.0	0.35
After admission of air	1.2	0.38	4.5	0.25	6.0	0.60	11.5	0.50

Note. The values of S_λ behind a KS-14 light filter are quoted in relative units based on the criterion of density $D = D_0 + 0.85$.

evacuation of emulsions, S_λ increased by a further factor of 1.5 and on subsequent admission of air it fell and virtually attained the initial value. The nitrone **7** also induced an increase in spectral sensitivity (by a factor of 5). It is striking that the joint activity of supersensitisers **4** and **7** exceeded the influence of evacuation. Thus their activity is not restricted solely to the inhibition of the reactions with oxygen and water. However, on exposure of evacuated light-sensitive layers containing the nitrone, their sensitivity nevertheless increased by a further factor of 1.5. This result as well as the decrease in S_λ for light-sensitive layers with supersensitiser **7** after the admission of air apparently indicate the incomplete inhibition of secondary reactions with participation of oxygen and water by the nitrone **7**.

Attention should be drawn to the fact that neither evacuation nor the introduction of individual supersensitisers ensured the maximum increment in the light sensitivity of photographic emulsions. A superadditive increase in the spectral sensitivity of an emulsion was attained only when supersensitisers **4** and **7** were employed jointly. There was then no evacuation effect. Thus the experimental data presented confirmed the hypothesis that oxygen and moisture influence the self-desensitisation reactions of electron-accepting dyes and indicate the ability of supersensitisers to inhibit secondary reactions involving oxygen and water protons.

Whereas the greater influence on S_λ compared with evacuation, in the case of the supersensitiser of the first kind **4** can be accounted for by the formation of a 'spacer' between the dye and AgHal, which effectively inhibits the self-desensitisation reactions in stage 1 of Scheme 1, another explanation is possible for nitrones.

In experiments on the regression of the latent image during the storage of exposed specimens with *C,N*-diphenylnitron at an elevated temperature and humidity, the appearance of a sensitometric wedge on the undeveloped emulsions has been observed.^{76, 132} The formation of visual densities is definite evidence for the occurrence of processes involving the intensification of the latent image. Thus the nitrone has a reducing function. The nitrone **7** belongs itself to the class of compounds which are difficult to oxidise, but its hydrolysis product — phenylhydroxylamine — has reducing properties. A 'reductive' mechanism, involving the latensification of the latent image, can therefore be considered as a variant of the supersensitising activity of nitrones. This results in a decrease in the probability of stage 1 (Scheme 1). The supersensitisation of infrared photographic materials by reductants has been discussed.^{135, 136} According to the authors of these publications, the infrared dye is oxidised on the surface of AgHal to radical-cations, which intensify the desensitisation processes by electron capture. The reductant (for example, ascorbic acid) reduces the radical-cations to the dye, promoting a decrease in desensitisation.

When secondary chemical dye self-desensitisation chemical processes are considered, attention is concentrated on the inhibition of stages 1–5 (Scheme 1). The recombination reactions of the electrons captured by the dye and oxygen with the dye holes (stages 6 and 7) have been examined to a significantly lesser extent. On the other hand, the recombination processes can also contribute to the self-desensitisation of dyes. It may be that the role of supersensitisers of the first and second kind consists also in

the inhibition of the recombination processes. In particular the reducing function of nitrones may involve the acceptance of a dye hole and hence the inhibition of stages 6 and 7 (Scheme 1), *i.e.* nitrones or their hydrolysis products can function in accordance with Gilman's hole capture mechanism.⁸² The difference between the approaches of the present author and Lenhard *et al.*¹³⁵ to the 'reductive' mechanism of supersensitisation concerns only the question of the origin of the infrared dye radical-cations; thus Muentert¹³⁵ believes that the radical-cations are formed in a dark process during the oxidation of the dye on the AgHal surface, whereas the present author believes that it occurs during the spectral sensitisation photochemical reaction.

VI. Self-supersensitisation of infrared dyes

Infrachromatic dyes with saturated cyclic groups in the polymethine chains belong^{137, 138} to the class of highly effective spectral sensitisers. The photographic effectiveness of such dyes has been attributed in a number of studies^{139–141} to hydrophobic protection by the saturated cyclic groups of the polymethine chain of the dyes against oxygen and water protons. The increase in the photographic activity of the infrachromatic dyes as hydrophobic alkyl groups accumulate in the chain has been demonstrated in relation to the thiatetracarbocyanines **23–26**.^{139, 141}

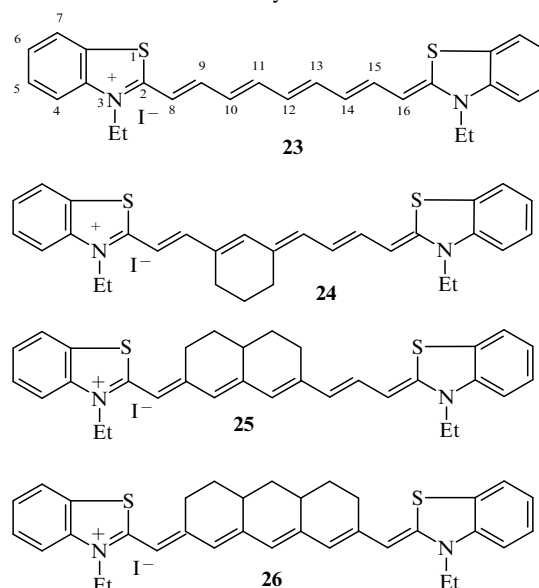


Table 4 presents results obtained on a monodisperse AgBr(I) emulsion with cubic microcrystals ($l = 0.27 \mu\text{m}$). The photographic activity of cyanines has been studied both individually and in the presence of supersensitisers of the first (the phosphine **4**) and second (the nitrone **7**) kind. The spectral (S_λ) and intrinsic (S_i) sensitivities of the photographic emulsions are quoted in relative units. The sensitivity of the emulsion without a dye has been adopted as unit S_i , whilst the sensitivity of photographic emulsions sensitised by dye **23** unsubstituted in the chain adopted as unit S_λ .

Table 4. The influence of the cyclic groups in the polymethine chain of thiatetracarbocyanines on the effectiveness of spectral sensitisation.

No. of experiment	Supersensitiser + dye	S_λ (KS-14)	S_i (S3S-22)
1	Unsensitised emulsion	—	1.0
2	23	1.0	0.3
3	4 + 23	2.0	0.4
4	4 + 23 + 7	3.5	0.5
5	24	2.0	0.4
6	4 + 24	5.0	0.45
7	4 + 24 + 7	7.0	0.55
8	25	4.0	0.5
9	4 + 25	10.5	0.55
10	4 + 25 + 7	20	0.6
11	26	6.0	0.5
12	4 + 26	18	0.6
13	4 + 26 + 7	40	0.6

Note. The values of S_λ and S_i have been obtained at pAg 7.4 from the criterion of density $D = D_0 + 0.85$ at a colour temperature of the light source of 2850 K.

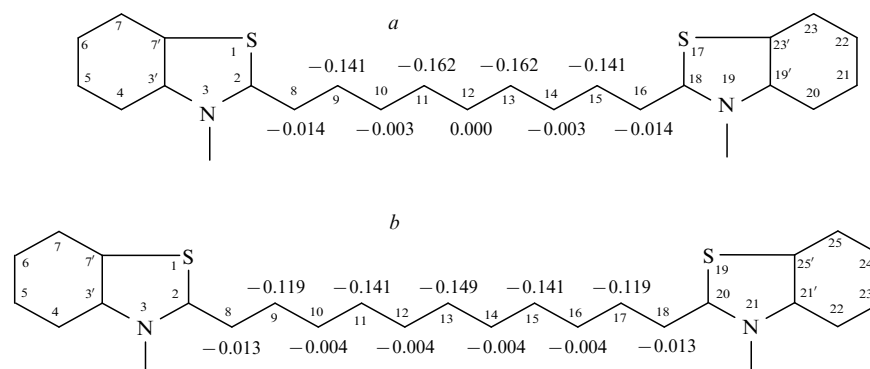
It follows from Table 4 that, with increase in the number of cyclic groups in the polymethine chain of the dyes from one (dye **24**) to two (dye **25**) and three (dye **26**), the spectral sensitivity due to the individual dye increases relative to the unsubstituted thiatetracarbocyanine **23** by factors of 2, 4, and 6 respectively (cf. experiments 2, 5, 8, and 11 in Table 4). The desensitising activity of the dyes diminishes in the same series of compounds (by a factor of 1.1–2.0) (cf. the values of S_i obtained in experiments 2, 5, 8, and 11). It is striking that the influence of cyclic groups on S_λ is significantly greater than on S_i .

The introduction of the supersensitiser of the first kind **4** promotes an increase in the spectral sensitivity of emulsions, which becomes more marked as cyclic groups accumulate in the chain (cf. the values of S_λ obtained in experiments 3, 6, 9, and 12 in Table 4), as a result of which the sensitivity of the emulsions with the **26** + **4** composition exceeds by a factor of 18 the sensitivity of those with the thiatetracarbocyanine **23** alone. Under the same conditions, the intrinsic sensitivity increases only by a factor of 2. The supersensitising activity of the nitron **7** is also determined by the number of hydrogenated bridges in the polymethine chain and reaches a maximum for dye **26** with three rings. Similar results have been obtained also on emulsions with the supersensitiser of the first kind **6**.¹⁴¹ The regular features of the influence of cyclic groups in the chain are retained in the series of

substituted thiapentacarbocyanines.^{132, 141} The greater influence of supersensitisers and cyclic groups on S_λ than on S_i confirms the difference, already discussed, between the dye desensitisation and self-desensitisation processes. According to the data presented, the supersensitising activity of cyclic groups in the dye chains is retained also in emulsions containing the supersensitisers of the first kind **4** and **6**, which themselves reduce the self-desensitisation of dyes as a consequence of the insulation of the latter from AgHal and promote thereby a more effective manifestation of the inhibiting activity of the hydrophobic saturated rings. The additional increase in spectral sensitivity in the presence of the hydrophobic supersensitiser of the second kind **7** can also be accounted for by the increase in the protective functions of the hydrophobic bridging groups in the presence of *C,N*-diphenylnitron. The hydrophobic nitron probably insulates additionally from oxygen and water the part of the dye chain which is not protected by the cyclic groups. This can explain the increase in the effectiveness of the nitron as rings accumulate in the chain, because the hydrophobic protective effects are then, as it were, added together. A contribution by the 'reductive' mechanism is possible.

It has been suggested^{132, 141} that the photographic activity of dyes with bridging groups should be manifested when the groups are in those positions in the polymethine chain where there is an excess π -electron density of the dye molecule which has captured an electron (in $\text{Dy}^{\cdot-}$). The probability of electron transfer to oxygen is a maximum at precisely these sites. When these sites are shielded by saturated groups, which hinder the approach of oxygen and especially water molecules, the probability of the dye self-desensitisation reactions should diminish. According to the molecular diagram (Fig. 29) of the distribution of π -electron density, constructed on the basis of LCAO MO quantum-chemical calculations in the Hückel approximation, the excess electron density in $\text{Dy}^{\cdot-}$ is concentrated in the 9-, 11-, 13-, and 15-positions in the polymethine chain of the thiatetracarbocyanine. Indeed, the introduction of two or three hydrogenated bridges at sites with the highest π -electron density (the 9-, 11-, and 13-positions for dye **25** and the 9-, 11-, 13-, and 15-positions for dye **26**) leads to a significant increase in the spectral sensitivity of the photographic emulsions. The value of S_λ for photographic emulsions with dye **24**, containing a saturated excess group in other positions in the chain (10, 12), where there is no excess electron density, is greater by a factor of 2 than for emulsions with the unsubstituted dye **23**. Presumably in this case the hydrophobic protection by the cyclic group extends not only to the sites to which it is attached but also to the neighbouring 11-position.

The distribution of π -electron density in the thiapentacarbocyanine molecule is also illustrated in Fig. 29. The highest π -electron density in $\text{Dy}^{\cdot-}$ is concentrated in the 9-, 11-, 13-, 15-, and 17-positions in the outer polymethine chain. According to experimental data,^{132, 141} the introduction of the β, β -dimethyltri-

**Figure 29.** Molecular diagrams for the distribution of π -electron density in the polymethine chain of thiatetracarbocyanine (a) and thiapentacarbocyanine (b).

methylene hydrophobic bridges in the 9- and 11-positions and in the 9-, 11-, 15-, and 17-positions (dye **1**) also increases the photographic activity of these dyes in the presence of supersensitisers compared with the thiapentacarbocyanine unsubstituted in the chain.

It is striking that cyclic bridging groups in the chains of thiatetra- and thiapentacarbocyanines decrease the catalytic effect of the dyes on the oxidation of latent image centres, *i.e.* the regression of LIC at elevated temperatures and humidities. Fig. 30 presents data taken from Mikheeva¹³² for the thiatetracarbocyanines **23**–**26**. The decrease in catalytic activity with increase in the number of rings in the chain is associated with the hydrophobic protection of the chain, already discussed, and hence with the inhibition of the reactions presented in Scheme 1. Thus, if it is assumed on the basis of the results that cyclic groups do indeed play the role of the hydrophobic protectors of the chain, one may speak of a new phenomenon — the self-supersensitisation of infrared dyes under the influence of saturated bridging groups.¹⁴¹ It is essential to note that one is dealing with the self-supersensitisation of dyes different from that considered by Collier,¹⁴² according to which the self-supersensitisation of *J*-aggregates of dyes is effected by dyes in the molecular form *via* the hole-acceptance mechanism.

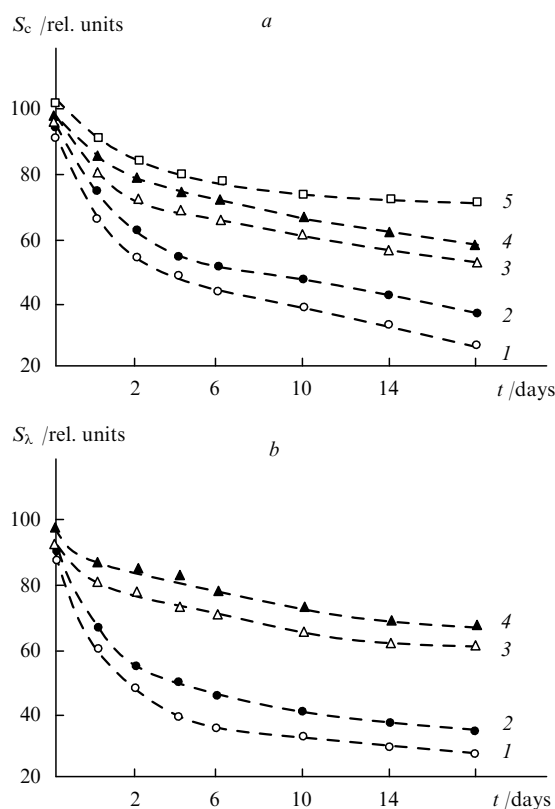


Figure 30. Variation of the intrinsic (S_e) (a) and spectral (S_λ) (b) sensitivities of photographic emulsions sensitised by the thiatetracarbocyanines **23** (1), **24** (2), **25** (3), and **26** (4) and of photographic emulsions without a dye (5) (28 °C, 78% humidity).

VII. Conclusion

The data examined indicate convincingly that the secondary chemical oxidation processes, or, in photographic terminology, the desensitisation processes play a very important role in the establishment of the sensitivity of infrared photographic materials. The desensitisation in the region of absorption by the dye (self-

desensitisation) then exceeds the desensitisation in the region of absorption by the silver halide. The self-desensitisation can actually determine the effectiveness of the spectral sensitisation itself. The oxidative mechanisms and the kinetics of the self-desensitisation processes are determined by the positions of the energy levels of the dyes relative to the energy bands of AgHal and also relative to the local surface levels.

It is striking that the infrared dye may play the role of an oxidation catalyst in the secondary processes. In a general sense, the vacant molecular orbitals of π -conjugated systems such as the molecules of polymethine dyes can therefore participate in the catalysis of the oxidation reactions of photographically active species. The role of oxygen and water protons is very important in these processes. To use a picturesque expression, one may say that the infrared photographic material, as it were, 'breathes' after photoexcitation. The silver atoms (the latent image precentres) are burnt up in the oxidative flame blown up by the infrared dye itself.

The supersensitisation processes reduce to a large extent to the inhibition of the secondary self-desensitisation reactions, *i.e.* the inhibition of the oxidation reactions of the products of the primary photochemical reaction. The ways in which oxidative processes are inhibited can be extremely diverse. They are determined both by the properties of the spectral sensitisers and by the type of the emulsion, so that the supersensitisers may be compounds with significantly different properties. There is a possibility of the self-supersensitisation of dyes as a result of the introduction into their molecular structure of self-desensitisation inhibitors. For example, dyes with the polymethine chain 'protected' to the maximum extent are promising. This can be achieved either by introducing hydrophobic substituents into the chain or by the 'truncation' of the outer polymethine chain when part of the chromophore chain is incorporated in heterocyclic rings. The use of various supersensitisers and their mixtures makes it possible, in principle, to eliminate fully the secondary oxidative processes and to approach thereby the limiting relative quantum yield of the spectral sensitisation. The greatest increment in spectral photosensitivity should then be expected for infrared photographic materials with a sensitisation zone longer than 1000 nm. Indeed, the effectiveness of the spectral sensitisation in the IR region with $\lambda \approx 1000$ nm has been increased by a factor of 100 and made to approach the values for the visible region of the spectrum^{5, 102} despite the fact that the level of the photoexcited electron in the thiapentacarbocyanine, used as the spectral sensitiser, is located approximately 0.7 eV deeper than the bottom of the AgBr conduction band.

One should note that the problem of the effectiveness of the spectral sensitisation of the direct positive process, based on the oxidation of pregenerated silver centres, is diametrically opposite to the problem of the effectiveness of the negative process already considered. Whereas in negative emulsions one is dealing with the inhibition of secondary oxidation reactions, in direct positive emulsions the supersensitisation is actually associated with the acceleration (promotion) of secondary oxidation reactions. In order to accelerate the oxidation of silver by dye holes, it is necessary either to introduce additional hole-transferring agents or to create conditions for the preferential adsorption of dyes on the centres containing silver particles which catalyse the development. Oxidative hole processes may intensify when the infrared dyes form extended *J*-aggregates. The formation of infrared dye *J*-aggregates on AgHal has been observed.^{143, 144} The promotion of electron capture reactions requires catalysis of electron transfer to oxygen and the water protons with the aid of additionally introduced electron-accepting compounds. Questions concerning the supersensitisation of direct positive emulsions have been examined, for example, by Belous *et al.*¹⁴⁵ and Steiger and Reber.¹⁴⁶

In conclusion, attention must be drawn to the following factor. In previous studies on spectral sensitisation, attention was concentrated on the primary spectral sensitisation step, on the effectiveness of which the effectiveness of the entire spectral

sensitisation process was assumed to depend. On the other hand, the effectiveness of the primary step was considered from physical standpoints, namely from the standpoint of the relation between the electronic levels of the photoexcited dyes and the electron bands of AgHal. Although secondary reactions were also taken into account in this approach, a secondary role was nevertheless attributed to them, *i.e.* their influence depended significantly on the probability of the primary process. On the other hand, in the chemical approach discussed here, the most important role in the establishment of the photographic parameters of the process is assigned to the secondary reactions. The primary spectral sensitisation step is treated as a surface oxidation-reduction reaction of the photoexcited dye with the silver ions,¹⁴⁷ which is virtually equally probable for the majority of the adsorbed dyes. Thus the problem of spectral sensitisation may be transferred from the class of 'purely physical' problems to the class of chemical problems, reducing to the search for effective ways of the inhibition, or, conversely, the promotion of the secondary oxidation reactions. The new chemical approaches have made it possible to expand the region of spectral sensitisation approximately to 1500 nm.¹⁴⁷

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Principles of the electronic structure of complexes of non-transition elements

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Abstract. The results of quantum-chemical calculations of electronic structures of complexes of non-transition elements are surveyed. Their X-ray emission and X-ray photoelectron spectra are analysed. General principles of the electronic structure of these complexes are established. It is shown that the effective participation of partially or completely occupied valence np^m orbitals of the central atom A of AL_k complexes in the formation of delocalised MOs, the negligibly small contribution of vacant nd orbitals to the bonds with ligands, the valence inertness or rather low contribution of occupied Ans^2 orbitals (except for $2s^2$ AO) to the valence MOs, and the initiation of multiple bonds (in the electronic structure of complexes) due to covalent or hypervalent π -interactions involving only $2p$ (but not $3p$, $4p$, etc.) atomic orbitals are the most significant factors influencing the electronic structure of non-transition element compounds. The concept of d orbitals and hypervalent bonds is criticised. The bibliography includes 130 references.

I. Introduction

The essence of the problem of the electronic structure of non-transition element compounds is quite simple. The main task is to find out what valence orbitals of central atoms (A) in the complexes AL_k ($k \geq 1$) of non-transition elements participate in the formation of bonds with ligands (L) described by delocalised molecular orbitals (MO).

In ionic compounds of alkali and alkaline earth metals, the leading part is played by the ns^1 and ns^2 orbitals; in other complexes of these metals, the contributions of the np orbitals should also be taken into account (especially in complexes formed by A^{II}). The physicochemical nature of the majority of compounds of Group I and II metal is too specific, and its analysis is beyond the scope of our review.

The electronic structures of complexes of Group III and IV non-transition elements can be described fairly adequately in

terms of the Ans and Anp orbitals and usually correspond to the traditional concept of sp^m -hybridisation of the basis AOs, especially in the case of boron and carbon complexes. The electronic structures of complexes of aluminium, silicon and their analogues with coordination numbers above 4 are more complicated.

The problem of describing the electronic structures of complexes of Group V–VIII non-transition elements is even more complicated, because the ground states of atoms of these elements contain one or more electron pairs localised in the valence ns and np AOs (in this case, the total number of valence electrons in an atom is greater than the number of valence orbitals, which is equal to four). At this point, the problem branches. The structures of the valence shells of the simpler molecules such as HF, HCl, H_2O , H_2S , NH_3 or PH_3 , in which the chemical bonds are mostly formed by unpaired Anp -electrons, are relatively simple; problems arise in determining the contributions of the occupied Ans^2 orbitals to the valence MOs and in solving the problem of hybridisation of the basis ns and np orbitals of the central atom.

The problem of describing an electronic structure is the most complicated in the case of higher compounds of Group V–VIII non-transition elements. The term 'higher compounds' is used in relation to molecular systems in which the oxidation state of a non-transition element A exceeds the number of unpaired np -electrons in the ground state of the atom, while the number of the unpaired Anp -electrons alone is insufficient to ensure that all the A–L bonds in the complex AL_k are two-electron two-centre interactions. The term 'higher compounds' cannot be regarded as appropriate, and its use can be justified only in striving for short presentation. According to this terminology, not only compounds of elements in the maximum oxidation states (Cl^{7+} , S^{6+} , etc.) are referred to as higher compounds, but also those in which the A atom is in a lower oxidation state (for example, complexes of formally trivalent chlorine ClO_2^{1-} or tetravalent sulfur, SO_3^{2-}).

Undoubtedly, the key role in the formation of bonds with ligands in the higher complexes of non-transition elements belongs to the valence np^m orbitals of the central atom. Therefore, the main point in studying the electronic structures of these compounds is to elucidate the degree to which the vacant nd orbitals and ns^2 orbitals occupied in the ground state of the central atom participate in the delocalised valence MO.

The problem of the description of electronic structures of complexes of non-transition elements has a long-standing history. Three stages, not separated from one another (in time or in the essence of the problems solved), can be distinguished, namely, empirical, semiempirical and non-empirical periods. The name of

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the last stage is conventional; this stage combines theoretical *ab initio* calculations of the electronic structures of non-transition element complexes carried out by the SCF and MO LCAO methods, by the methods of scattered waves and by X_α -discrete variation; experimental studies of these complexes by X-ray emission and X-ray photoelectron spectroscopy; coordinated studies of electronic structures using both X-ray spectroscopy and the MO theory and general theoretical approaches to the problem.

II. Empirical concepts

In our review, attention is concentrated on the electronic structures of higher compounds of Group V–VIII non-transition elements. A considerable part is occupied by the discussion of the nature of, and the reasons for the differences between, the electronic structures of complexes formed by elements of the Second Period and by elements of the Third and higher Periods.

To describe the electronic structures of higher compounds of Group V–VIII non-transition elements of the Third and subsequent Periods, two alternative concepts were developed as early as the 1950s. According to one of them (the concept of *d* orbitals), it is assumed that both the ns^2 and np^m orbitals of the central atom A occupied in the ground state and its vacant *nd* orbitals are involved in the binding with ligands.^{1,2} The bonds between the atom A and the ligand were described by multi-centre MOs formed according to the requirements of group theory with efficient participation of the *ns*, *np* and *nd* orbitals of atom A (strictly specified for each type of molecular symmetry) and the corresponding group orbitals of the ligands. This concept was based on the idea of $sp^m d^n$ hybridisation of valence orbitals of the central atom and made it possible to pass from the canonical delocalised MOs to equivalent localised MOs, *i.e.* to describe the electronic structure of an AL_k complex by a certain set of two-electron two-centre covalent A–L σ - and π -bonds. A fairly important role has been allocated to the allowance for the symmetry of the complex. The vacant *nd* orbitals of the central atom able to participate in the σ - or π -interactions with the ligand orbitals were strictly specified in conformity with the symmetry point group. The concept of *d* orbitals (sometimes referred to as the theory of complete hybridisation) has been presented clearly and systematically in monographs.^{3,4}

The second concept is the concept of hypervalent bonds. It is based on the idea of three-centre four-electron interactions proposed by Pimentel and Rundle^{5–7} and assumes that the bonds of atom A with ligands are mostly formed through the valence np^m orbitals of the central atom. The ns^2 -electrons are used only in some cases, whereas the vacant *nd* orbitals remain valence-inactive and do not participate in the A–L bonds. The electronic structure of an AL_k complex is described as a set of two-electron two-centre covalent A–L bonds involving the unpaired electrons of the A atom and three-centre four-electron (hypervalent) $L_{(1)}-A-L_{(2)}$ bonds involving the paired np^2 -electrons or, more rarely, the ns^2 -electrons of the A atom.^{8,9} In the case of complexes with central atoms in the highest oxidation states (SF_6 , PF_5 , *etc.*), the Ans^2 orbitals are assumed to participate necessarily in the valence MOs. The concept of hypervalent bonds (or the theory of three-electron bonds), the history of its development and its numerous consequences have been considered in monographs.^{3,4,10}

In the 1950s and 1960s, the concept of *d* orbitals occupied a leading position in the theory of electronic structure of compounds AL_k of non-transition elements. This can be explained retrospectively as follows. In those years, theoretical studies were mainly concerned with complexes of transition metals. Their electronic structures have been modelled using the crystal field theory, the ligand field theory and the MO theory including various versions of calculation procedures. The theory of the electronic structures of compounds of non-transition elements has remained the Cinderella of quantum chemistry and has been ‘fascinated’ by the successes in the rapidly progressing theory of electronic structure of transition metal complexes. Researchers

believed that the electronic structure of AL_k cannot present anything conceptually new, interesting or significant compared to that of complexes ML_k of transition metals M; the electronic structures of the latter have usually been described using all the valence AOs [*ns*, (*n*–1)*d*, *np*] with allowance for the symmetry requirements. Therefore, views on the electronic structures of AL_k have largely resulted from the groundless transfer of the general ideas of the theory of the electronic structure of ML_k to coordination compounds of non-transition elements and from the wide use of the statement that the principles of the electronic structure of two types of complexes — AL_k and ML_k — are close and even identical. Moreover, the concept of *d* orbitals has been supported by many experimenters, who have searched and seemingly ‘found’ evidence supporting participation of the *And* orbitals in the electronic structures of AL_k and in the A–L bonds.

However, at that time, some arguments in favour of the concept of hypervalent bonds were found. Syrkin and Linnet^{11–13} noted that *d* AO make fairly low contributions to the electronic structures of non-transition element complexes. They stressed that the characteristics of those vacant *d* orbitals of non-transition element atoms that should be included in the basis set of atom A cannot be theoretically estimated with a sufficient accuracy. Furthermore, since the *And* orbitals in AL_k can be delocalised near the ligands, the problem of *d* AOs is generally less significant than it had seemed initially. The requirement that the number of hybrid orbitals of the central atom in an AL_k complex should coincide with the number of two-centre bonds and the *a priori* judgment of the multiplicity of the A–L bonds cast special doubt upon the concept of *d* orbitals. Therefore, the setback of these ideas observed in the last few years is surprising.¹⁴

In the 1960s, it was believed that the problem in question could be solved by systematic quantum-chemical calculation of the electronic structures of non-transition element complexes. Both concepts are ‘one bone and one flesh’ in MO theory. Within the framework of these concepts, the electronic structures of AL_k complexes can be described using both delocalised MOs and localised two- and three-centre MOs. Therefore, since the middle 1960s, quantum-chemical calculations have been used systematically to model the electronic structures of various AL_k complexes in various approximations of the MO theory.

III. Semiempirical calculations of molecular orbitals

The greatest number of calculations for AL_k complexes have been carried out by semiempirical MO LCAO methods. Owing to computational difficulties only few *ab initio* calculations for complex multi-electron and multi-centre AL_k compounds, based on the Hartree–Fock–Roothaan (SCF MO LCAO) method with fairly complete and balanced atomic basis sets, were performed at that time.

The MO LCAO calculations have provided extensive information; these results have been presented fully and comprehensively and in a clear and systematic form in the review by Dyatkina and Klimenko.^{15 †}

The review begins with comments on the calculations of spatial and energy characteristics of vacant *nd* orbitals of isolated atoms and atoms in a ligand field. These calculations did not give an answer to the direct question, whether the *nd* AOs can participate in bonds, but indicated that the spatial characteristics of *d* orbitals (unlike those of *s* and *p* AOs) can vary over wide limits, from very diffuse to contracted orbitals, depending on the valence state of the atom. The calculations for excited states of atoms also have not clarified the situation, although they have provided useful information on the energies of excitation from the

† We advise those who are interested in the problem of vacant AO, to read this brilliant review, which was published in 1973 and marks the completion of a stage in the development of the quantum-chemical views about electronic structure of non-transition element compounds.

ground states of atoms to their valence states in which the nd orbitals are occupied by electrons and on the orbital energies of these electrons.¹⁶

Based on the results of semiempirical MO LCAO calculations for various AL_k complexes, the authors of the review made some conclusions that seemed the most reliable and significant at that time. These conclusions can be outlined as follows.

The populations of d AOs are substantial but not more than 0.5–1 electron. According to the theory of localised bonds, the populations of d orbitals are postulated to be large integer values, and thus the contributions of these orbitals are overestimated twice or even more. The contributions of d orbitals are greater in compounds with high valences of the central atom (such as SO_2 , SO_4^{2-} , SF_6) and increase with an increase in its formal valence. In addition, the contributions of d AOs increase with the decrease in the degree of ionicity of bonds (in oxygen compounds they are greater than in fluorine compounds, the number of ligands being the same). No considerable donor-acceptor $Lp_\pi \rightarrow Ad_\pi$ interactions can be detected even in those cases where these interactions are allowed from the symmetry viewpoint. The allowance for d orbitals influences the calculated properties of molecules in different ways. For example, it should be noted that the calculation of dipole moments and inversion barriers requires that d orbitals be necessarily included in the basis set of AOs even for elements of the Second Period (although in this case, the contributions of d AOs are lower than those for atoms of the Third Period elements). However, the MO energies are less sensitive to the expansion of the basis set due to d AOs. Therefore, it would be hasty to judge the role of d AOs based only on the analysis of one or several molecular properties, the more so as an increase in the influence of d AO on a particular characteristic is not always proportional to the increase in the electron population of d AO. It is necessary to analyse a variety of properties that respond in different ways to the inclusion of d orbitals in the atomic basis set. The results of calculations do not identify any correlations between the contributions of d AOs to the MOs and electronic characteristics of the atom and, hence, they do not make it possible to discuss the variation of the nd AO populations as a function of the position of the non-transition element in the Periodic Table.

In addition to the MO LCAO semiempirical calculations, the maximum overlap method has also been used to study the role of d orbitals and the extent to which they participate in the hybrid orbitals of tetrahedral oxo-anions. The tetrahedral hybrid orbitals

$$\varphi = \alpha\chi_s + \beta\chi_p + \gamma\chi_d,$$

were calculated with allowance for the contributions of both d_σ and g_p components. The $s^1p^3d^n$ electronic configurations of the central atoms were estimated from the relations $l:m:n = \alpha^2:\beta^2:\gamma^2$. The results of the calculations showed that the relative d -contribution to the electron population of atom A varies over wide limits (from 0.02 for BrO_4^- to 0.3 and 0.4 for ClO_4^- and AsO_4^{3-}), but it is always several times smaller than the d -contribution to the electron population of central atoms M in analogous tetrahedral oxo-anions formed by transition metals (for example, VO_4^{3-} , CrO_4^{2-} , MnO_4^-).

In other studies,^{18–21} the problem of vacant d orbitals of non-transition element atoms has been discussed in terms of the results of semiempirical calculations of valence electron density distribution in two- and multi-atomic fluorides, chlorides, oxides and complexes of the $AX_{k-n}Y_n$ type with coordination numbers of 3, 4 and 6. The calculations were carried out by the MO method in the zero differential overlap (ZDO) approximation. It was found that d orbitals play an insignificant role in the formation of chemical bonds between central atoms and ligands. In particular, it was shown that the fact that the energies of dissociation of the Si, P, S and Cl monofluorides are larger than those of the C, N, O and F monofluorides is not associated with the role of d orbitals of the atoms of Third Period non-transition elements but is due to the specificity of their s and p AO, i.e. to specific spatial and energy characteristics of $A3s$ and $A3p$ orbitals.

The statistical theory of Thomas–Fermi atoms²² has also been invoked to the solution of the problem of vacant $3d$ orbitals of the atoms of non-transition elements of the Third Period. It was shown that these atoms, unlike those of elements of the Second Period, have no states occupied by electrons and characterised by the orbital quantum number $l = 2$; the states with $l = 2$ can be occupied only in the case of cations. The electron populations of the states with $l = 2$ is determined by the degree of ionisation of the atom; both lower and upper limits to the degree of ionisation exist. Depending on its effective positive charge, the same central atom can have, or not have, occupied $3d$ states. A particular degree of ionisation of the atom is necessary but insufficient for the $3d$ AO to be occupied, because the extent of this occupation is also determined by the nature of the donor of valence electrons. Thus the population of the $3d$ AO of chlorine in ClF_2^+ is close to zero (0.05 a.u.), despite the considerable degree of formal ionisation of the chlorine atom ($q_{Cl} = +1.18$ a.u.), which is favourable for the population of its $3d$ AO. Apparently, this is due to the low electron-donating ability of fluorine atoms ($q_F = +0.09$ a.u.).

In recent years, semiempirical calculations have been seldom used to solve the problem of vacant d orbitals; sometimes, the results of these calculations are compared with the photoelectron spectroscopy data for the corresponding complexes.^{23,24} The results of the latter indicate that d orbitals contribute significantly to the valence electron structures of higher sulfur fluorides, silicon oxo-complexes, etc.

Nevertheless, the conclusion that the problem of d orbitals cannot be solved adequately within the framework of the semiempirical approach is beyond any doubt.¹⁵ The semiempirical MO LCAO calculations exaggerate the role of d orbitals and give a wrong picture of the electron density distribution; they are of little use for the description of the qualitative variation of d -contributions in various series of molecules, do not prove in any way the real participation of the And AOs in the A–L bonds and give so great a scatter of the calculated values of d -populations that attempts to extract unambiguous information from them are hopeless. These calculations confuse rather than clarify the problem of outer d orbitals.

In the early 70s, it seemed that the final solution of the nd AO problem would become possible as a result of systematic non-empirical calculations for a great number of complexes; generalisation of experimental values for a broad range of molecular properties; thorough analysis of the regularities in the variation of these properties and establishing correlations between the molecular properties and calculated characteristics of the contributions of d orbitals to the valence molecular orbitals in the electronic structures of complexes. However, the first studies along these lines have already shown that counting on the non-empirical approach to the estimation of the role of d AOs in the valence electronic structures of complexes of non-transition elements also has no prospects.

IV. Non-empirical MO calculations and X-ray spectra of complexes

The need to determine reliably the populations of the outer (vacant) atomic orbitals in an explicit form and their contributions to various molecular properties imposes stringent requirements upon the MO method used for the calculations. The non-empirical SCF MO LCAO method and X_σ -methods meet these requirements best of all. However, even fairly legitimate calculations carried out for AL_k complexes in terms of these methods have not resulted in the solution of the nd AO problem.

The following approach is normally used to solve the nd -AO problem in terms of *ab initio* and X_σ -methods. The participation of And orbitals in $\sigma(d_\sigma-s, p_\sigma)$ or $\pi(d_\pi-p_\pi)$ bonds with ligands is set depending on whether or not the inclusion of the nd_σ and nd_π orbitals into the atomic basis set results in the calculated energies of single-electron MO approaching the corresponding experimental values and/or in a decrease in the total energy of the molecular

system. The electron population of the *And* orbitals in the complex is estimated from the same viewpoint.

Unfortunately, no unambiguous conclusions have been drawn from the results of calculations for complexes of non-transition elements accumulated over the past two decades.

The results of some of the *ab initio* SCF MO LCAO and SCF SW X_α -calculations attest to an appreciable electron population of the *And* orbitals in the complexes studied,^{15,25–29} whereas according to other calculations, this population is equal to zero.^{30–32} In addition, the results published for the same compounds are sometimes at variance with one another. For example, the population of the atomic *And* orbitals in SF₆ has been found²⁹ to be 1.2e[–], whereas according to another study,³² the electron structure of SF₆ is hypervalent and is described without participation of the 3*d* orbitals of the central atom. X_α -calculations for SF₆ has led Condlii and Johnson³¹ to the conclusion that the S3*d* orbitals remain virtually unoccupied.

In a typical case, the inclusion of *nd* AOs into the atomic basis set leads to a slight decrease in the energy of those MOs which can contain *nd* AOs [for example, $e_g(\sigma)$ and $t_{2g}(\pi)$ MO in an octahedral complex]. However, this decrease in the MO energies does not occur for all *nd* exponents, and, besides, the energies of the rest of the single-electron MOs can increase when the *nd* AOs are taken into account. Therefore, despite the fact that allowance for the *And* orbitals is believed to result (according to the variational principle) in a decrease in the total energy of the molecule, this is due to the change in the energies of the Coulomb and exchange interelectron interactions rather than to stabilisation of single-electron energy levels.³³ This paradoxical result is reproduced in the *ab initio* and SCF SW X_α -calculations for SF₆, SeF₆, TeF₆ and PF₅ complexes and for the isoelectronic series PO₄^{3–}, SO₄^{2–}, ClO₄[–].

The results of SCF DV X_α -calculations^{34–38} of the electron structures of many halides and halo-anions of non-transition elements AL₄^{*p*–} (*p* = 0–3) including SF₆, SF₅Cl, SF₅O[–], etc. in the basis of numerical Hartree–Fock functions indicate that the chemical bonds and many properties of AL₄^{*p*–} complexes (reactivity, geometrical structure, stability and its dependence on the charge for series of isoelectronic complexes) are due to the formation of multi-centre MOs. The latter consist of all the valence *s* and *p* orbitals of the central atom and the ligands, which are transformed in terms of the corresponding irreducible representations for the symmetry groups of the complexes under study.^{34–38} Most of the calculations do not confirm the participation of the vacant *And* orbitals in the bonds with ligands. In particular, when the electronic structure of SF₆ has been calculated in the *s,p* basis, good agreement between the calculated single-electron energy levels and the experimental ionisation potentials has been observed.^{34,37} The addition of the S3*d* orbitals to the Hartree–Fock basis did not change the order of the levels and did not result in significant improvement of the calculated single-electron MO energies with respect to the experimental values for the *d* exponent varied over a fairly broad range. However, it should be noted that in the case of TeF₆, good agreement between the calculated and experimental MO ionisation potentials is observed when the calculation is carried out with the *s, p, d* basis set of the central atom;³⁷ thus, a more adequate description of the sequence of MO energies in TeF₆ is achieved when the atomic basis is supplemented by the Te5*d* orbitals. Based on the results obtained by DVM X_α -calculations of the molecular orbitals of the SF₅O[–] anion, isoelectronic to SF₆, the increase in the multiplicity of the S–O bond has been explained by the fact that all the valence AOs of oxygen participate in binding with the AOs of sulfur to a greater degree than those of fluorine, without assuming the occurrence of the S3*d* _{π} –O2*p* _{π} interactions.³⁸ Perhaps, the higher multiplicity of the bonds in the SO₄^{2–} tetraoxo-anion is also not associated with the S3*d* _{π} –O2*p* _{π} interaction.

In the non-empirical calculations, the agreement between the calculated and experimental geometric parameters of a complex (type of the polyhedron, bond lengths, bond angles) are often used as a criterion for elucidating the role of *nd* AOs. In this case, one

must take care whether the addition of *nd* functions of the central atom to the atomic basis set improves the geometry (*i.e.* the agreement with experiment). Again, some *ab initio* results imply that *And* orbitals exert only insignificant influence on the optimum geometrical parameters of sulfur halides and show their low electron population.³⁹ Conversely, some other calculations attest that *d* functions need to be taken into account in order to describe adequately the geometric structures of molecules of this type and, in these cases, the populations of *And* orbitals are found to be high.^{40–43} However, in this case, too, some interesting peculiarities have been found. Firstly, the large population of *nd* AOs has a substantial influence on the energies of Coulomb and steric repulsions and does not lead to enhancement of the d_π – p_π interaction. Moreover, in addition to the *d*-contribution, the second-order Jahn–Teller effect, caused by the presence of low-lying excited states with appropriate symmetries, can also be a crucial factor influencing the geometric (and electronic) structures.⁴¹ Secondly, the addition of *d* functions results in almost identical effects for complexes of elements of the Third Period (SF₄, SOF₂, SO₂F₂)⁴² and of the Second Period (NO₂⁺, NO₂[–], NO₃[–], NO, etc.).⁴³ In both cases the addition of 3*d* orbitals to the basis set improves the geometry and reduces the total energy of the molecule, which correlates well with the population of *d* AOs. The higher the formal valence of the central atom, S or N, the larger the effect of stabilisation due to *d* AOs. Similarly, non-empirical calculations for homonuclear polyhedral molecules P₄, As₄, P₈ and As₈ using a pseudopotential and a two-exponent basis set indicate that the expansion of the basis set due to vacant *nd* AOs makes it possible to explain the fact that the P₄ and As₄ clusters are more stable than the 2P₂ and 2As₂ systems, respectively.⁴⁴ It was noted⁴⁴ that the crucial factor determining the higher stability of P₄ with respect to 2P₂ is the increase in the electron population of *d* AOs from 0.06 to 0.10. However, very close values have been found⁴⁵ not only for the As₂ and As₄ clusters but also for N₂ and N₄, although the hypothetical N₄ molecule is known to possess much higher energy than 2N₂.

Here we encounter a quite typical situation, which has been analysed in detail in the review by Bochvar *et al.*⁴⁶ Up to now, while we discussed the problem of *d* orbitals, we proceeded from the assumption of real atomic *d* orbitals in the sense in which the valence *s* and *p* orbitals in a molecule are real. Then we assumed that non-zero electron populations of *d* AOs can serve as an actual criterion and a measure for their participation in the A–L bonds. Note in this connection that Coulson⁴⁷ has suggested that two cases should be distinguished: (1) the contribution of *d* AOs is large (about 0.5–1 electron or more), then one can speak of their real participation in bonds; (2) the contribution of *d* AOs is small, then they act as polarising functions, and the discussion of their populations makes no particular sense. The second case represents a different aspect of the problem of *d* orbitals, based on the fact that the radial parts of *d* functions obtained in MO calculations by minimising the total energy of the molecule (with allowance for the variation of the AO exponents) differ markedly from the radial parts of *d* orbitals of isolated atoms (they are more contracted) and approach the radial parts of the corresponding valence *s* and *p* AOs; for example, 3*d* → 3*s*, 3*p*.^{48,49} This strong contraction is observed in all cases and is independent of the *d*-population and of the effective charge on the atom in a molecule. These altered *d* orbitals are no longer related directly to vacant valence orbitals of the atom. Now they have a different meaning: they should be regarded as certain corrections in *ab initio* calculations that take into account polarisation of valence *s* and *p* AOs upon the formation of bonds and make the total molecular wave function more precise. Mulliken has suggested that the populations of these outer $d_{\sigma,\pi}$ AOs should be regarded as the populations of those valence σ,π AOs, which they polarise.⁵⁰

If we assume that the role of *d* orbitals reduces to corrections for calculations, then we should find out what the relative significance of these corrections is in the calculations of the electronic structures of compounds of Second and Third Period

elements. The inclusion of $3d$ functions into the central atom basis sets in the calculations for compounds of elements of the Second Period is always accompanied¹⁵ by their strong compaction ($3d \rightarrow 2s, 2p$), non-zero electron populations, and by a decrease in the total energy of the molecular system.^{15, 46} Thus, in the case of *ab initio* calculations for compounds of elements of the Second Period, the atoms of which have no valence d orbitals at all, the $3d$ functions also act as effective corrections. Using numerous nitrogen and phosphorus compounds as examples, Bochvar *et al.*⁴⁶ demonstrated convincingly that the role of d -type corrections in the calculations for compounds of Second and Third Period elements is approximately the same; in these two cases, d -populations are close and the effects of d AOs on various molecular properties are quite comparable in magnitude. For quantum-chemical reasons, the participation of d orbitals in the electronic structures of compounds of Second Period elements has never been considered to be necessary; therefore, the second ('correction') aspect of the allowance for d orbitals seems to be more and more preferable. It can be assumed that in *ab initio* calculations for compounds of Third Period elements, the role of d -type orbitals is to counterbalance the defects caused by an inadequate sp basis set.⁵¹

Expansion of a basis set increases the number of variational parameters; consequently, the test function becomes more flexible and, hence, the total energy of a molecular system always decreases (owing to the variational principle). Basis set expansion is typical of quantum-chemical calculations. The expansion of the basis set in terms of the Roothaan method makes it possible to obtain (within the specified accuracy) the wave functions corresponding to the Hartree–Fock limit. However, the total energy of a molecular system is less sensitive to the basis set expansion than other electronic characteristics and, therefore, it cannot be a reliable criterion for establishing the Hartree–Fock limit in calculations by the Roothaan method (the virial theorem and the Gelman–Feynman theorem are used as additional criteria).⁵² In addition, the stability of a molecular system cannot be fully explained in the Hartree–Fock terms; for this purpose, the correlation energy and core effects should also be taken into account.^{53, 54}

It is clear from the above that it is impossible to determine correctly the populations of d AOs and, hence, to solve the problem of vacant d orbitals in terms of merely quantum-chemical Hartree–Fock–Roothaan (HFR) calculations (even the most accurate) with a multi-exponential expanded and balanced basis set, without allowance for configuration interactions (CI) (which is typical of most of *ab initio* calculations). Apparently, only in terms of the multi-configuration approximation for a self-consistent field (MC SCF), will an adequate estimation of d -contributions to various properties of the systems under consideration be possible. (All the above is also true for the little-studied problem of occupied *Ans*² orbitals.) Within the scope of the MO LCAO method, the problem of outer d AOs is additionally complicated because, as noted above, the term d AO is used with two meanings, and there is no clear criterion to distinguish between the 'real d AOs' and 'polarising d functions'.¹⁵ It should also be borne in mind that the question of outer d AOs arises only in the MO LCAO approximation, which is most extensively used now but is not the only one existing.

Since the early 70s, ultrasoft X-ray spectroscopy has been used actively in studies dealing with the problem of vacant d orbitals. X-Ray emission spectra provide vital information on the electronic structures of complexes; relative energies of all valence MOs and the contributions of the majority of atomic orbitals to them can be found in this way. According to the dipole selection rules, those MOs that contain contributions of the $3s$ and $3d$ orbitals of atoms of the element under investigation ($3s \rightarrow 2p$ and $3d \rightarrow 2p$ transitions) can be manifested in the L -spectra of elements of the Third Period (Cl, S, P, Si, *etc.*).^{55–57} The complete sets of X-ray fluorescence spectra for a large number of chlorine and sulfur compounds have been studied most extensively in this

respect.^{58–63} In the opinions of the researchers cited, these spectra unambiguously indicate that $3d$ orbitals of chlorine and sulfur atoms do contribute to chemical bonds. These and other similar data on ultrasoft X-ray spectroscopy covering a wide range of non-transition element compounds are believed to be indisputable experimental evidence for effective participation of $A3d$ -electrons in chemical bonds.

However, another viewpoint also exists. Analysis of X-ray emission L -spectra of sulfur and chlorine compounds⁶⁴ permits one to distinguish several reasons for the complicated and inconsistent structure of emission CL - and SL -spectra. One of them is decomposition of a substance during recording of the spectrum with both the primary excitation of the spectra by electrons and the secondary excitation by photons. Experimental (emission CL -spectra of ClO_4^-) and theoretical (SCF SW X_α -calculations of ClO_4^-) data confirm that a large fraction of the intensity of the low-energy band in the X-ray emission L -spectrum is due to products of decomposition of ClO_4^- .⁶⁵ It should also be taken into account that under the conditions of recording X-ray emission spectra, interaction of a compound studied with the copper anode surface is possible. Finally, one more reason lies in the fact that in the assignment of spectral bands, the superimposition of short-wave radiation with higher-order reflection on the recorded spectrum (for instance, the sixth order reflection of $L_{\alpha_{1,2}}$ - and L_{β_1} -lines of copper) is not monitored (and, hence, is not taken into account).

The theory of X-ray emission spectra is largely based on the single-electron orbital model. The X-ray lines in a multi-electron system are assumed to be due to a transition between two states having particular electron configurations and described by the Hartree–Fock method. In the one-particle approximation (in the approximation of 'frozen' orbitals) in which the relaxation effects are ignored, the Hartree–Fock orbitals of the ground state of the molecular system under study are used in calculations of excited states. The results of SCF *ab initio* calculations of the fine structures of X-ray emission spectra for SO_2 , CS_2 , SCO and Cl_2 molecules have been reported,⁶⁶ and it has been found that the orbital model has only limited utility for the interpretation of the spectra due to the presence of significant correlation effects. In the $CK\beta$ -spectra of CS_2 and SCO , high-intensity transitions from the lower antibonding molecular orbitals (which are vacant in the ground state) have been detected. To explain the presence of short-wave satellites, the X-ray re-emission mechanism (inelastic non-shifted scattering) has been invoked. Previously, high-intensity short-wave satellites have been found in K - and L -spectra of boron, carbon and sulfur and interpreted as re-emission transitions from excited levels.^{61, 67–69}

Thus, the data of ultrasoft X-ray spectroscopy cannot be regarded as indisputable evidence for the participation of d orbitals of the central atoms in the chemical bonds in complexes of non-transition elements, since experimental results often disagree with one another and their traditional interpretation is incorrect and unambiguous. It is significant that stricter investigations carried out more recently have a different character. The energies and intensities of the X-ray L -emission of the central atom for PO_4^{3-} and ClO_4^- have been measured experimentally and calculated theoretically by the SCF SW X_α method.⁷⁰ The inclusion of $A3d$ orbitals in the basis set improves the agreement between the calculated and measured intensities of lines and energies of X-ray spectral transitions (the transition energies were calculated using the transition state approximation) but has almost no influence on the orbital energies of the PO_4^{3-} and ClO_4^- ground states. This implies that $A3d$ orbitals participate only slightly in their electronic structures. A study of the electronic structure of $POCl_3$ carried out by X-ray and X-ray photoelectron spectroscopy and by SCF MO LCAO, MINDO/3 and SCF SW X_α *ab initio* calculations⁷¹ has shown that the contribution of d orbitals of the phosphorus and chlorine atoms to the occupied valence molecular orbitals of $POCl_3$ is relatively small.

The results of studies on the effect of the chemical shifts of the emission X-ray lines for compounds of non-transition elements do not lead to unambiguous conclusions on the role of *d* orbitals either. The chemical shifts of the emission K_{α_1} - and K_{β_1} -lines of xenon in the X-ray spectra of XeF_2 , XeF_4 , Li_4XeO_6 , NaHXeO_4 and Na_4XeO_6 with respect to similar xenon lines in a hydroquinone clathrate have been measured.⁷² These chemical shifts were compared with the Mössbauer isomer shifts of xenon for the same compounds.¹²⁹ The results were interpreted in terms of the model of valence electron configuration of a free effective ion. X-Ray transition energies and the electron density on the nucleus in this ion were calculated by the Dirac–Slater method. The question of whether the $\text{Xe}5d$ orbitals participate in the bonds with ligands remained open; however, the workers⁷² pointed to the possibility of this participation in the electronic structures of high-valence oxygen compounds of xenon. Analogous results have been obtained somewhat earlier for a number of iodine compounds.^{73, 74}

Based on the most general statements of the MO theory and the perturbation theory, Shustorovich has justified theoretically the fact that *And* orbitals do not make a significant contribution to the valence MOs of complexes of non-transition elements.^{33, 75, 76} An indispensable condition for effective electron interaction between the valence orbitals of the central atom and the ligands is proximity of their orbital energies. In the second order of perturbation theory (for non-degenerate levels), the energy of stabilisation for a bonding MO

$$\varphi = C_A \chi_A + C_L \chi_L,$$

(where C is a variational parameter) is determined by the formula

$$\Delta E_{\text{AL}} \sim \frac{\beta_{\text{AL}}^2}{|\alpha_A - \alpha_L|}, \quad (1)$$

where α_A and α_L are the Coulomb integrals characterising ‘self-consistent’ energies of χ_A and χ_L orbitals (in those approximations of the MO theory in which an effective single-electron Hamiltonian is used), β_{AL} is the resonance integral determining the energy of interaction between the χ_A and χ_L AOs and proportional to the overlap integral S_{AL} . In the atoms of Group IV–VIII non-transition elements, the energies of *nd* orbitals are 10–15 eV higher and the energies of *ns* orbitals are 10–20 eV lower than those of *np* orbitals. This indicates that the contributions of *ns*, *np* and *nd* orbitals of atom A to the bonds with ligands are necessarily inequivalent. In typical cases, the energies of the valence orbitals of ligands are somewhat lower than the energies of the *Anp* orbitals. Therefore, the vacant *And* orbitals prove to be too high-lying for them to interact efficiently with the occupied valence orbitals of ligands. For the same reason, the occupied *Ans*² orbitals are not always able to participate in the bonds with ligands: their energy is often too low compared to those of the valence orbitals of the ligands. Generally, the high *ns*–*np* and *np*–*nd* separation energies for atom A attest to a crucial role of the *Anp* orbitals in the formation of the electronic structure of AL_k complexes and to much smaller contributions of the *Ans*² and, especially, *And* orbitals to the valence MOs. Characteristic properties of coordination compounds of non-transition elements can be calculated without using the *nd* orbitals of the central atom, which act as polarisation corrections for the orbital basis set.^{26, 77–80} As a whole, the general theoretical ideas prove unambiguously that the vacant *And* orbitals make no significant contribution to the valence MOs in the electronic structures of non-transition element complexes; the role of the occupied *Ans*² orbitals is less clear.

While researchers discuss the problem of *d* orbitals (more precisely, when a large contribution of *d* AOs to the electronic structure of a complex is stated *a priori*), they often refer to the symmetry criteria and stress that for any point group of symmetry of an AL_k complex, there are always some orbitals among the *And* AOs that belong to the same irreducible representations as the

valence orbitals of the ligands. Therefore, σ or π interaction of the *And* orbitals with the ligand orbitals is always possible to one or another extent.

Later, this thesis has been made more precise in the following way:⁸¹ the *d* AOs make a real contribution to the electronic structures of complexes in the case where these orbitals, being included in the basis set, form, in conformity with the symmetry properties, new bonding MOs upon interaction with the AOs of the ligands (for example, *e* orbitals in MX_4 or *t*_{2g} and *e*_g in MX_6); otherwise, they should be regarded as polarising corrections. However, firstly, non-empirical calculations show that *d* AOs are by no means always involved in bonds, even when it is possible from the symmetry viewpoint. Secondly, the results of a comparative study of the influence of *d* functions in various calculation versions[‡] imply⁸² that *d* orbitals with appropriate symmetry are not more important than the rest of *d* AOs. Besides, in calculating the electronic structure of the excited state of a molecule, the criterion of symmetry is less significant for the selection of *d* AOs than the optimisation of an additional diffuse *d* AO needed to describe MO of the Rydberg type. Finally, what is the most essential, the allowance for *d* AOs is not necessary for the construction of the appropriate number of MOs in the electronic structure of an AL_k complex of a certain symmetry. For example, when only one *ns* and three *np* orbitals of the central atom are available, one can construct, resorting to the AOs of ligands, six equivalent MOs corresponding to the canonical orbitals (*a*_{1g}, *t*_{1u}, *e*_g) of an octahedral complex; having only three *np* orbitals of the central atom at disposal, one can construct four equivalent MOs corresponding to the canonical orbitals (*a*₁, *t*₂) of a tetrahedral complex.³³ In the former case, the *e*_g MO is a non-bonding ligand orbital, while in the latter case, this refers to the *a*₁ MO.

Thus, since the results of nonempirical calculations of the electronic structures of non-transition element complexes are ambiguous and the interpretation of the ultrasoft X-ray spectroscopy data is by no means irrefragable, it is still an urgent task to describe the general principles of the electronic structures of non-transition element complexes and to answer the basic theoretical question: what valence orbitals of central atoms do participate in the formation of delocalised MOs?

V. X-Ray photoelectron spectra of compounds of non-transition elements

The most significant studies accomplished in recent years reveal the inconsistency of the concept of *d* orbitals. However, the existing theory of the electronic structure of non-transition element complexes is still contradictory in some aspects and lacks inherent unity. Besides, there exists not only the problem of vacant *nd* AOs, but also the problem of occupied *ns*² AOs, and the latter has been quite little investigated until recently. Further development of the theory requires precise experimental studies on the electronic structures of these compounds.

Below we discuss the results of systematic studies of typical complexes of non-transition elements carried out by photo- and X-ray photoelectron spectroscopy, which are now the basic physical methods used to study occupied electron levels in free molecules and crystals.^{83–85} In appropriate points of the discussion, we present data from X-ray emission and Mössbauer spectroscopy, Auger electron spectroscopy and spectroscopy of internal conversion electrons. We include only those experimental results that have been obtained repeatably by various authors and virtually agree with one another, *i.e.* results that can be regarded as final. The discussion material covers compounds of Group IVA–VIIIA elements. The discussion is based in many respects on our own studies in which the parameters of the X-ray photoelectron

[‡] Using *d* functions of the central atom, appropriate from the symmetry viewpoint; with a basis set of the central atom incorporating *d* functions not corresponding to the criterion of symmetry; taking into account the full set of *d* functions in a balanced basis set.

spectra (XPS) of the valence band and inner levels of the central atoms were interpreted for the first time independently of the results of theoretical calculations on the electronic structures of the corresponding complexes. The analysis of line intensities was performed using photoionisation cross-sections and included systematic comparison of relative intensities. In the analysis of the energy positions of the lines, we used the energies of the valence orbitals and the core levels of the corresponding free atoms. As a result of these studies, X-ray electron criteria have been established that make it possible to estimate the degree of participation of vacant nd and occupied ns^2 orbitals of the central atom in the molecular orbitals of the A–L bonds.

1. Vacant And orbitals

To determine the degree to which nd orbitals of the central atom A participate in the valence MOs of non-transition element complexes from the parameters of their X-ray photoelectron spectra, two approaches have been used: analysis of the relative intensities of the XPS valence lines and of the energies of the inner levels of the A atom in these complexes.^{85,86}

At present, there are only a few reviews devoted to the analysis of the XPS of non-transition element compounds.^{85,87} In the majority of cases, the analysis of XPS and the interpretation of the electronic structure of complexes based on it are carried out resorting to the results of the corresponding non-empirical calculations. Most of these coordinated investigations seem to support the view on the considerable contribution of And orbitals to the electronic structure of complexes. This relates, first of all, to the most studied series of isoelectronic tetraoxo-anions,^{85,87,88} ClO_4^- , SO_4^{2-} , PO_4^{3-} and even to xenon fluorides.^{89,90}

However, apparently, the conclusions about the large contributions of d AOs based on the analysis of XPS are not quite correct. This is indicated not only by the fact that the results of some SCF calculations are in excellent agreement with XPS even without allowance for d AOs.

In fact, the valence XPS of tetrahedral oxo-anions ClO_4^- , SO_4^{2-} and PO_4^{3-} and many other oxo-anions^{85,87,91,92} contain identical numbers of bands and are quite similar to one another in the positions of bands and in their relative intensities. A typical example is provided by the X-ray photoelectron spectrum of the ClO_4^- , which is shown in Fig. 1a. In this spectrum, the two upper bands corresponding to the $1t_1$ and $3t_2$ MOs with the same electron population ($6e^-$) are close in energy and have almost

identical intensities. This means that these MOs consist of only $2p_\pi$ orbitals of the oxygen atoms, and there is scarcely any significant contribution of the And orbitals to the $3t_2$ MO (the contribution of And AOs to the $1t_1$ MO is forbidden from the symmetry viewpoint). Otherwise, the relative intensities of the two bands under consideration would have been markedly dissimilar owing to the different photoionisation cross-section of the nd levels of the atom A and the $2p$ levels of the oxygen atoms.

Analysis of the intensities of the two next bands corresponding to the $1e$ ($4e^-$) and $2t_2$ ($6e^-$) molecular orbitals does not permit one to distinguish unambiguously between the absence or the presence of a contribution from the And orbitals to these valence MOs, because this contribution is, in principle, allowed from the symmetry viewpoint for both $1e$ and $2t_2$ MOs composed of the $\text{Cl}3p$ and $\text{O}2p$ orbitals. However, the high intensity of these bands suggests that the And orbitals do not make any significant contribution with low ionisation cross-sections to them. In addition, the $1e$ and $2t_2$ MOs lie lower in energy than the $1t_1$ and $3t_2$ molecular orbitals and, therefore, a contribution of the fairly high-lying And orbitals to the $1e$ and $2t_2$ MOs is even less likely than their contribution to the $1t_1$ - and $3t_2$ MO, which contain no And AOs.

Further evidence for the absence of a contribution of the And orbitals to the valence MOs of the AO_4^{n-} oxo-anion is the fact that the structure of the upper energy bands in the valence XPS of tetrahedral oxo-complexes of transition metals MO_4^{n-} is absolutely different. The latter are isostructural and isoelectronic with AO_4^{n-} .^{85,87,91,92} The electronic structures of the M–L bonds in the oxo-complexes are described with allowance for the valence ns^2 and $(n-1)d$ orbitals of the central atoms M (Fig. 1b,c).

Similar conclusions can be drawn from the results of X-ray photoelectron studies of some other complexes of non-transition elements.^{93–97} A specific place in this series of studies is occupied by the study of Siegbahn,⁹⁷ who carried out a detailed analysis of the intensities of lines in the valence photoelectron spectra of SF_6 recorded with various types of ionising radiation (He-I, He-II) and concluded that the spectral parameters would have been different if the $3d$ orbitals of the sulfur atoms had played a significant role.

Thus, the intensities of XPS valence bands indicate that there is no $And_{\sigma,\pi} \leftarrow Lnp_{\sigma,\pi}$ donor-acceptor interactions involving vacant And orbitals in the electronic structures of non-transition element complexes. This was shown, for example, in the studies of SO_4^{2-} (without $\text{S}3d_\pi \leftarrow \text{O}2p_\pi$) or SF_6 (without $\text{S}3d_\sigma \leftarrow \text{F}2p_\sigma$), although from the viewpoint of the d orbital concept, the XPS studies should have revealed the participation of the nd orbitals of the central atom in the formation of delocalised valence MOs of the complexes.

Another X-ray electron confirmation of the fact that vacant And orbitals do not participate in the A–L bonds is the character of dependence of the energies of inner levels of the central atom A on its oxidation state (formal valence) in the complexes.

Based on the results of a systematic study of the X-ray photoelectron spectra of the inner levels of central atoms in many complexes of non-transition elements, it has been shown⁸⁶ for the first time that the variation of the energy and of the chemical shift of some inner level of atom A in a series of compounds formed by this element follow a linear dependence on its formal valence. For series including numerous compounds of a non-transition element, starting from the Third Period, for example, $\text{NaCl} - \text{NaClO}_4$ ($\text{Cl}2p_{3/2}$), $\text{KBr} - \text{NaBrO}_4$ ($\text{Br}3d_{5/2}$), $\text{KI} - \text{KIO}_4$ ($\text{I}4d_{5/2}$), $\text{CdS} - \text{Na}_2\text{SO}_4$ ($\text{S}2p_{3/2}$), $\text{CdSe} - \text{Na}_2\text{SeO}_4$ ($\text{Se}3d_{5/2}$), $\text{CdTe} - \text{H}_6\text{TeO}_6$ ($\text{Te}4d_{5/2}$, $\text{Te}3d_{5/2}$), no substantial deviations from linearity for the correlations: ‘energy of an inner level of A – the oxidation number of A’ have been found (Fig. 2). When the chemical shifts were calculated from the experimental E_b values, the binding energy of the inner level of the central atom in its compound with the lowest oxidation state is taken as the zero point. The results obtained for all the systems studied are alike: the binding energy and the chemical shift of the inner level of atom A increase linearly with increase in its oxidation number. Moreover,

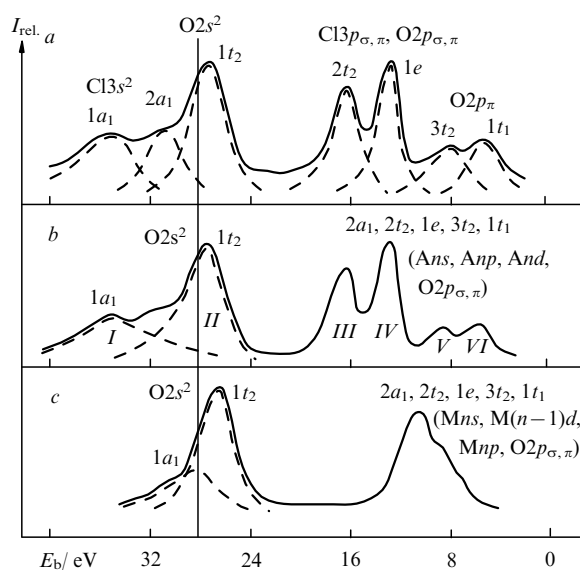


Figure 1. Valence band X-ray photoelectron spectra of tetrahedral tetraoxo-anions ClO_4^- (a), AO_4^{n-} (b), MO_4^{n-} (c). For numbers I–VI, see the text.

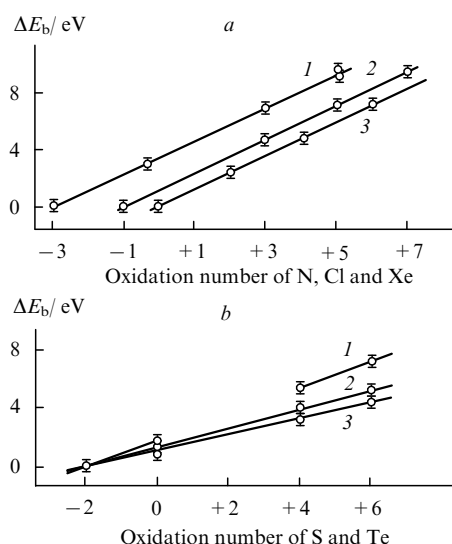


Figure 2. Chemical shifts for inner levels of atoms A as functions of their oxidation numbers.

a: N1s_{1/2} (1); Cl2p_{3/2} (2); Xe3d_{5/2} (3); b: S2p_{3/2} (1); Te3d_{5/2}; Te4d_{5/2} (3)

this 'linear effect' does not depend on the type of the inner level of the atom A (for example, Te3d_{5/2} and Te4d_{5/2}, Fig. 2).

This linearity was explained⁸⁶ as resulting from the low contribution of vacant *And* orbitals to the valence MOs of A–L bonds. Indeed, participation of vacant *nd* orbitals of the atom A in bonds with ligands (for example, with the 2*p* AO of oxygen in oxo-complexes) is possible only through a donor-acceptor mechanism with transfer of the valence electron charge from the occupied orbitals of ligands to the vacant *nd* orbitals of the atom A (*And* ← *Lnp*, 0:2), and this should have led to a relative increase in the electron charge on the atom A, to the corresponding decrease in the binding energy of its inner level, and to a deviation from the linear dependence described above up to its disappearance. This is why the 'linear effect' implies that the virtual *nd* orbitals of the central atom almost do not participate in the bonds with ligands in compounds of phosphorus, arsenic, antimony, sulfur, selenium, tellurium, chlorine, bromine, and iodine, *i.e.* of typical non-transition element of the Third Period and subsequent Periods. This conclusion is also strongly supported by the following facts. Firstly, the linear correlation between the binding energy and the chemical shift of the inner energy level of anion A holds for those compounds of a non-transition element, the electronic structures of which are known to contain no contribution of the *And* orbitals (Na₂S, CdS, S, see Fig. 2) and is extended in the same form to its compounds with high oxidation states (Na₂SO₃, Na₂SO₄) in which the concept of *d* orbitals suggests effective participation of *And* orbitals in the A–L bonds. Secondly, a similar linear dependence is also observed for nitrides and nitrogen oxo-complexes as well as for xenon

fluorides (see Fig. 2)^{98,99} in which the absence of any contribution of *nd* orbitals of the central atom to the bonds with ligands is beyond any doubt. Thirdly, in the series of coordination compounds of transition metals in which all the valence orbitals of the central atom including *M*(*n*–1)*d* AOs can participate in M–L bonds, the dependences of the inner level energies of the atom M on its oxidation state are complicated and non-linear; in this case, there is no linear correlation (or any other correlation, up to the 'star sky'), owing to the differences in the relative roles of the covalent M–L, donor-acceptor M ← L and dative M → L bonds in each particular ML_k compound.

2. Occupied *Ans*² orbitals with *n* ≥ 3

The problem of participation of *Ans*² AOs in A–L bonds in non-transition element complexes can be solved by studying their valence X-ray photoelectron spectra. For this purpose, one should find out whether the band of the quasiatomic *Ans*² level is retained in the spectrum or is missing due to the involvement of the *Ans*² orbitals in valence delocalised MOs of the complex.

Fig. 1 shows the typical valence X-ray photoelectron spectra for tetraoxo-complexes of non-transition elements AO₄^{m–} and transition metals MO₄^{m–} obtained for A = Cl, Br, I, S, Se, Te, As and M = V, Cr, Mn, Mo, W, Re.^{87,91,92} The traditional interpretation^{87,91} of the valence XPS of an AO₄^{m–} or MO₄^{m–} complex (*i.e.* the assignment of the bands to particular MO of the complex) is based on the results of semiempirical and non-empirical quantum-chemical calculations for the electronic structures of tetrahedral oxo-anions. In the spectrum of AO₄^{m–} (see Fig. 1b), high-energy bands I and II were assigned to the atomic O2s² levels (the 1a₁ and 1t₂ MO), bands III and IV were attributed to the 2a₁, 2t₂, and 1e molecular orbitals of the A–O σ-bonds formed upon interaction of the valence *Ans*, *Anp*, *And*, and O2*p* orbitals; finally, bands V and VI were assigned to the non-bonding O2*p*_π levels (the 3t₂ and 1e MOs, poorly resolved in energy). This assignment provokes serious objections for a number of reasons.⁹²

Firstly, the valence spectra of isoelectronic and isostructural (*T_d*) AO₄^{m–} and MO₄^{m–} tetraoxo-anions are absolutely different, and this is natural, because the valence electronic configurations of the central atoms A and M are different. However, within the region of O2s² levels, one should expect (from the viewpoint of the above interpretation) that the forms and energies of the X-ray photoelectron bands would be fairly similar if not completely alike. However, there is no similarity (Tables 1 and 2). The O2s-lines in the spectra of MO₄^{m–} are highly symmetrical (the asymmetry index is close to unity) and have virtually identical energies irrespective of the nature of the central atom. This means that in the MO₄^{m–} tetrahedral anions, the O2s² levels and the corresponding 1a₁ and 1t₂ MOs are very close in energy (the splitting energy Δ = 1–2 eV), which is in full agreement with the results of *ab initio* calculations¹⁰⁰ for the electronic structure of MO₄^{m–}. According to these calculations, the O2s²-electrons are quasiatomic and are not involved in the formation of bonds with the central atom. At the same time, in the spectra of AO₄^{m–}, the two bands with higher

Table 1. Valence bands in the spectra of tetraoxo-anions of nontransition elements/eV.

AO ₄ ^{m–}	<i>E_b</i> of line I (<i>Ans</i> ² , 2a ₁)	<i>E_b</i> of line II (O2s ² , 1a ₁ + 1t ₂)	Widths of lines I and II at the basis	<i>A</i> ±0.05	Levels of A– σ-bonds; O2 <i>p</i> _π levels				
					2t ₂	1e	3t ₂	1t ₁	line width at the basis
ClO ₄ [–]	36.0	28.6	18.0	0.6	18.3	15.2	10.5	8.6	13.8
SO ₄ ^{2–}	32.0	27.6	14.2	0.6	16.9	13.7	10.3	7.2	14.8
PO ₄ ^{3–}	30.5	27.1	13.4	0.5	16.0	12.0	7.2	9.1	15.9
SeO ₄ ^{2–}	30.8	27.2	12.8	0.7	17.8	12.9	9.1	–	–
AsO ₄ ^{3–}	31.0	27.1	12.0	0.6	16.7	13.1	10.1	10.1	12.0
IO ₄ [–]	29.8	26.5	14.4	0.5	17.6	12.0	8.7	8.7	14.4

Note. I, II are lines in Fig. 1; *A* the ratio of intensities of lines I and II.

Table 2. Valence bands in the spectra of transition metal tetraoxo-anions.

MO ₄ ^{m-} complex	O2s ² levels (1a ₁ + 1t ₂)				Levels of M–O σ-bonds; O2p _π levels	
	I	II	III	IV	I	II
CrO ₄ ²⁻	25.3	11.0	3.9	1.16	14.1–6.1	8.0
MoO ₄ ²⁻	25.2	10.8	3.2	1.00	14.4–6.0	8.4
WO ₄ ²⁻	25.2	10.6	3.2	1.00	13.8–6.6	7.2
ReO ₄ ⁻	25.4	8.0	3.6	1.04	13.4–5.8	7.6

Note. The following designations are used: I is the energy of a line /eV; II is the line width at the basis /eV; III is the width at the half-height /eV; IV is the asymmetry index.

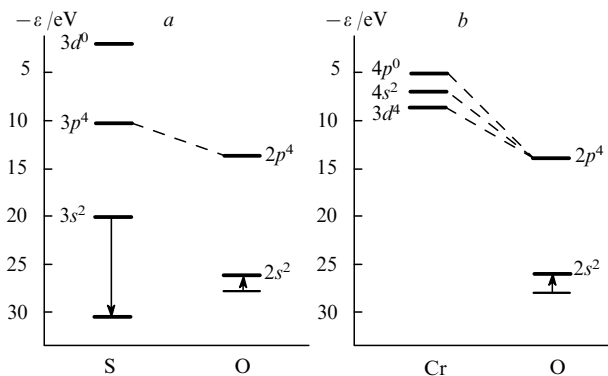
energies, which are assigned traditionally to the quasiautomic O2s² levels, have much more complex shapes. In conformity with the generally accepted views, the splitting energies for the 1a₁ and 1t₂ MOs calculated from the XPS parameters are relatively large ($\Delta = 5\text{--}6\text{ eV}$; in the case of ClO₄⁻, $\Delta = 7.4\text{ eV}$) and this is at variance with the low energy of splitting of the O2s² levels in MO₄^{m-}.

Secondly, if bands *I* and *II* (see Fig. 1b) were actually due to the O2s² levels in conformity with the generally accepted interpretation, the ratio of their intensities would be 1 : 3, since the ionisation cross-sections for the 1a₁ (2e⁻) and 1t₂ (6e⁻) O2s² levels are virtually identical (because their energies are close) and the ratio of their intensities is determined only by their electron populations, *i.e.* it is 1 : 3. However, in all valence XPS of the AO₄^{m-} complexes without exception, the ratio of the intensities of lines *I* and *II* is markedly larger and ranges from 0.5 to 0.7 (instead of the expected 0.33).

Thirdly, the energies of the O2s² levels in the MO₄^{m-} complexes are close to those of the O2s² level in the free oxygen atom (the vertical line at 28.5 eV in Fig. 1). If band *I* in the spectrum of AO₄^{m-} is attributed to the O2s² level, it is impossible to explain its substantial stabilisation, taking into account the negative effective charge on the oxygen atoms in AO₄^{m-} (as well as in MO₄^{m-}). The situation can hardly be saved by referring to the stabilisation by the crystal field of the positively charged cations (K) in the crystal structure of K_mAO₄ (in this case, this stabilisation would be also manifested in K_mMO₄).

The detailed analysis of the intensities and energies of the two bands with the highest energies (*I* and *II*) in valence XPS of AO₄^{m-} shows⁹² that the former band corresponds to the quasiautomic ns² level of the central atom A, which is not involved in the valence delocalised MOs and hardly participates in the bonds of the atom A with ligands; the latter band, like the corresponding band in the spectra of transition metal tetraoxo-anions, is due to the quasiautomic 2s² levels of the oxygen atoms (2a₁ and 1t₂ MOs). This interpretation (see Fig. 1a) eliminates simultaneously all the contradictions mentioned above and makes it possible to understand the characteristic features of the X-ray photoelectron spectra and the essential difference between these spectra of isostructural and isoelectronic tetraoxo-anions of non-transition elements and transition metals.

In fact, since the electronegativity of oxygen is higher than that of the central atom in the AO₄^{m-} complex (as well as in other oxo-complexes of non-transition elements and transition metals), a positive effective charge appears on the central atom and a negative charge appears on oxygen (it is also necessary to take into account the negative charges of the AO₄^{m-} and MO₄^{m-} anions themselves). This results in stabilisation of quasiautomic An_s² orbitals with respect to those in the free atom A and in destabilisation (to a markedly lesser degree) of the quasiautomic O2s² levels with respect to those in free oxygen atoms (Fig. 3a). This is why the highest-energy (~35 eV) band *I* in the valence XPS of AO₄^{m-} cannot belong to the O2s² levels but represents the quasiautomic ns² orbital of the central atom A, which is markedly stabilised (by 7–

**Figure 3.** Changes in the energy of quasiautomic orbitals upon the formation of oxo-complexes of a non-transition element (*a*) and a transition metal (*b*).

10 eV) with respect to the ns² orbitals of the free atom A. The same energy of stabilisation (up to 10 eV) of both the core and quasiautomic valence orbitals of the central atom A upon the formation of higher complexes has been pointed out by Siegbahn,^{83,84,97} based on the analysis of the parameters of numerous X-ray photoelectron spectra.

The energy separating bands *I* and *II* in the valence spectrum of AO₄^{m-}, which has earlier been regarded as the energy of splitting of the 1a₁ and 1t₂ O2s² levels, is actually the difference between the energies of the quasiautomic An_s² orbital and the O2s² levels and can vary over wide limits depending on the individual nature of the atom A (on the energy of the ns² orbitals in the free atom A) and on its formal valence.

Now we make an important comment. Whereas in the oxo-complexes of non-transition elements AO₄^{m-}, the quasiautomic ns² orbital possesses the greatest binding energy in the valence band, in the case of fluorides AF_k^{m-}, it is the F2s² levels that are characterised by the greatest binding energy in the valence band. This is due to the fact that the energy of the 2s² orbital of F is much greater (37.8 eV) than that of the 2s² orbital of O (28.5 eV); therefore, the quasiautomic An_s² orbital, which is highly stabilised in the electronic structure of the fluorides AF_k^{m-}, cannot 'outrun' in energy the F2s² levels, which are somewhat destabilised. Therefore, in the valence XPS of both MF_k^{m-} and AF_k^{m-}, the lines with the highest energies correspond to the F2s² levels.

The valence ns² orbitals of the central atom in the electronic structure of MO₄^{m-} (unlike those in AO₄^{m-}) are incorporated in the valence MOs (their energies being markedly higher than those of the O2s states) and thus participate efficiently in the M–L bonds. Therefore, the quasiautomic 2s² levels of oxygen have the greatest binding energies (Fig. 3b) in the valence band and, hence, the valence XPS of a MO₄^{m-} complex does not and cannot contain a band similar to band *I* in the spectrum of AO₄^{m-}.

The degree of ionicity of bonds and consequently the effective negative charge on the ligands in MO₄^{m-} are higher than those in isoelectronic AO₄^{m-} complexes, since the electronegativities of atoms M are markedly lower than those of A. Therefore, one can expect that the O2s-line in the valence XPS of MO₄^{m-} should be destabilised (with respect to 28.5 eV) to a greater extent than that in the case of AO₄^{m-}. Experimental studies (Fig. 1) have completely confirmed this assumption.

The ratio of intensities of lines *I* and *II* (see Fig. 1b) in the valence spectrum (if the former is assigned to the An_s² state) should not be equal to 0.33, but should vary, as is actually observed in experiments, depending on the nature of the central atom A (Cl, Br, I, S, Se, P, or As), on the corresponding changes in the ionisation cross-sections¹⁰¹ of the valence ns² levels of these atoms and on the integral intensity of band *I*, if the ionisation cross-section of the O2s² level and the integral intensity of band *II* corresponding to it are constant.

The energies of the ns^2 orbitals of the central atoms A in the series $\text{ClO}_4^- - \text{BrO}_4^- - \text{IO}_4^-$, $\text{ClO}_4^- - \text{SO}_4^{2-} - \text{PO}_4^{3-}$, *etc.* depend on the electron populations (effective charges) of atoms A; the latter, in turn, are determined by the chemical individuality of the particular atom A, *i.e.* by the energy of ns^2 AOs in the free atom and by the orbital electronegativity. The energy of an ns^2 AO is also influenced by the total electrostatic charge of the complex, by the difference between the orbital electronegativities of the central atom and the ligands and by some other factors. In addition, according to the interpretation being developed, the energies of the $\text{O}2s^2$ levels vary in the same series. In particular, in the series $\text{ClO}_4^- - \text{SO}_4^{2-} - \text{PO}_4^{3-}$ and $\text{BrO}_4^- - \text{SeO}_4^{2-} - \text{AsO}_4^{3-}$, the energy of stabilisation of the Ans^2 level increases with respect to the ns^2 energy in the free atom A; this corresponds to a decrease in the total charge on atoms A in these series due to the decrease in the ns and np orbital ionisation potentials of A. The destabilisation of the quasiatomic $\text{O}2s^2$ and $\text{O}2p^2$ levels in relation to their energies in a free oxygen atom increases in the same series; this is due to the increase in the valence electron density on the oxygen atoms in AO_4^{m-} . Similar regularities caused by the same reasons are observed in the series $\text{ClO}_4^- - \text{BrO}_4^- - \text{IO}_4^-$ and in analogous series of tetraoxo-anions of sulfur, selenium, phosphorus, arsenic, *etc.*

This new interpretation of valence XPS of oxo-complexes of non-transition elements is versatile and covers not only AO_4^{m-} tetraoxo-anions but also the rest of known oxo-complexes with different numbers of coordinated oxygen atoms, with another symmetry, *etc.* In this case, additional arguments supporting this interpretation appear.

Firstly, the quasiatomic nature of Ans^2 AOs is confirmed by the fact that the intensity of a particular line in valence XPS of compounds of the same non-transition element is almost the same; this is also true for those compounds in which the Ans^2 orbitals are known not to participate in A–L bonds, for example in the $\text{ClO}_4^- - \text{ClO}_3^- - \text{ClO}_2^- - \text{ClO}^- - \text{Cl}$ series. If an Ans^2 orbital did participate in A–L bonds, the intensity of the Ans^2 -line (normalised with respect to a certain core level) would not remain constant irrespective of the structure of the oxo-complexes, owing to different degrees of mixing of Ans^2 and $\text{O}2p$ orbitals in the valence MOs.

Secondly, as the number of coordinated oxygen atoms in an oxo-complex decreases, the ratio of the intensities of Ans^2 - and $\text{O}2s^2$ -lines in its valence spectrum increases proportionately. This type of behaviour is characteristic only of quasiatomic electron levels.

Thirdly, if the line with the highest binding energy in valence X-ray photoelectron spectra of oxo-anions and other complexes of a non-transition element actually corresponds to a quasiatomic Ans^2 state, then the energy of this level, like that of any inner level, should increase linearly following an increase in the oxidation state of the atom A. Besides, the 'sensitivity' of the binding energy of a quasiatomic Ans^2 level to the number of ligands with a higher electronegativity (oxygen atoms in this particular case) coordinated to it should be higher than that of other inner levels of the atom A with the same symmetry. In other words, it should be expected that the rate of increase in the ns level binding energy will be higher than those for $(n-1)s$, $(n-2)s$, *etc.* levels in the series of compounds with increasing oxidation state of the central atom, because the ns level is the most outer level among those considered. In the valence XPS of chromium, sulfur, selenium, and arsenic compounds with various oxidation states, the binding energies for ns^2 levels of atoms A have been determined. This is illustrated by Fig. 4, which shows, as an example, the dependence of the chemical shift of the $\text{Cl}3s^2$ level on the oxidation state of chlorine. Moreover, this Figure contains analogous relationships for the chemical shifts of the $K(1s)$ and $L(2s)$ levels of chlorine based on the data of Siegbahn.⁸⁴ It can be seen that the binding energy of the $\text{Cl}3s^2$ level actually increases linearly with an increase in the oxidation number of chlorine atoms, the rate of its growth being much greater than those for the energies of core levels.

The fact that the energies of the valence ns^2 levels of central atoms A behave in the same way as the core $1s^2$ and $2s^2$ levels (as

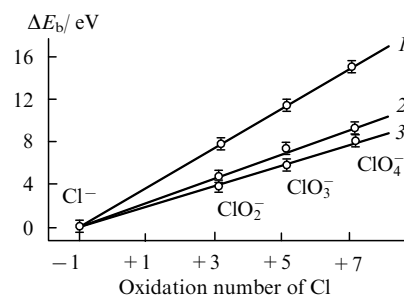


Figure 4. Dependence of the chemical shifts of $\text{Cl}ns^2$ levels on the oxidation number of the chlorine atom.

(1) $\text{Cl}3s$, (2) $\text{Cl}1s$, (3) $\text{Cl}2s$.

regards a nearly linear variation of their energies as functions of the formal valence of the atom A) seems very important for the solution of the problem of participation of Ans^2 orbitals in the formation of the electronic structure of a non-transition element complex. According to the generally accepted views, only valence-inactive quasiatomic electron levels behave in this manner.

Thus, the analysis of the parameters (energies and line intensities) of valence band X-ray photoelectron spectra of oxo-complexes of non-transition elements of the Third and subsequent Periods (especially, comparison of these parameters with those for oxo-complexes of transition metals) leads to the following conclusion: the occupied ns^2 orbitals of the central atom in AO_k^{m-} , unlike those in MO_k^{m-} , are involved in bonds with ligands to only a small extent. The Ans^2 -electrons remain quasiatomic and are markedly stabilised compared to the corresponding electrons in free atoms.

Further X-ray-electron evidence for the valence inactivity of the occupied Ans^2 orbitals is the linear dependence of the inner level energy of the central atom on its formal valence, which has been considered above.⁸⁶ In fact, the occupied ns^2 orbitals of the central atom A could participate in two-centre two-electron (covalent) bonds with ligands by the dative mechanism, $\text{Ans}^2 \rightarrow \text{L}np$ (2:0) due to the vacant valence orbitals of the ligands or by forming three-centre four-electron (hypervalent) $\text{L}_{(1)}np \leftarrow \text{Ans}^2 \rightarrow \text{L}_{(2)}np$ bonds due to the valence orbitals of the ligands with unpaired electrons. In both cases, this would be accompanied by the transfer of electronic charge from the central atom to the ligands, a decrease in the electronic charge on atom A, a corresponding increase in the binding energy of its inner level and by the disturbance of the linearity discussed above. This is due to the fact that, since the penetration ability of the ns orbitals in atom A is higher than that of the np orbitals, their participation in the bonds with ligands should 'uncover' the nucleus of the atom A to a greater extent and, in conformity with the effect of internal shielding, this should stabilise more efficiently the core levels of the atom A. The linear variation mentioned above of the binding energy of the $\text{Xe}5d_{5/2}$ level in the series of xenon fluorides is spectacular in this respect. It is almost obvious that not only the $\text{Xe}5d$ AOs do not participate in the electronic structure of xenon fluoride, but the occupied $\text{Xe}5s^2$ orbitals [$\sigma_g(\text{XeF}_2, D_{\infty h}$ symmetry), $a_{1g}(\text{XeF}_4, D_{4h}$ symmetry), $a_{1g}(\text{XeF}_6, O_h$ symmetry)] also remain quasiatomic^{89,90} and refer to fully symmetrical irreducible representations; the hypervalent bonds $\text{F}-\text{Xe}-\text{F}$ involve only the valence $5p$ orbitals of the xenon atom.

In general, the 'linear effect' indicates that the vacant And and occupied Ans^2 orbitals of the central atom A do not make any significant contribution to the A–L bonds and that these bonds are formed via consecutive involvement of valence orbitals of the atom A of only one type, namely, the np AOs. The linear increase in the energy of the inner level is due to the variation in the quantitative characteristics of the participation of np -electrons in the bonds with ligands following the change in the oxidation state of the central atom A. In the electronic structures of AL_k complexes,

the *And* orbitals remain virtual, while the occupied *Ans*² orbitals prove, as a rule, to be valence-inactive and remain quasiatomic.

Thus, taking into account the differences in the shielding effects, in the penetration ability, in single-electron energies, and in the electronegativities of valence *ns*, *np*, and *nd* orbitals of the atom A, one can conclude that if the *And* and (or) *Ans*² orbitals did really participate in the A–L bonds, the linear dependence of binding energy (*E*_b) of the inner level of the atom A on its oxidation state would be necessarily violated. Experimental evidence for the fact that the dependence of *E*_b of the inner levels always deviates from linearity when *Ans*² orbitals are effectively involved in the valence MOs will be presented below. Analogous facts concerning *And* orbitals have not yet been found, but SCF MO LCAO *ab initio* calculations of the electronic structures of the ClO₄[−], SO₄^{2−}, and PO₄^{3−} oxo-anions²⁶ indicate that when the A3*d* functions are included in the atomic basis set, the effective charge on the central atom A sharply decreases compared to that obtained for a purely *sp* basis set (for example, from +2.4 to +0.8 for Cl in ClO₄[−]). Therefore, the electron density on the atom A increases, and this should markedly diminish the binding energy of its inner levels, *i.e.* should result in abnormal values of *E*_b, deviating from the linear dependence.

The present concept of small contribution of the valence *Ans*² orbitals to the MOs of A–L bonds has also been supported in other experimental and theoretical studies, which are yet few in number. The results of HFR non-empirical calculations^{26,88} show that in the electronic structures of ClO₄[−], SO₄^{2−}, PO₄^{3−} and ClO₃[−] oxo-complexes, the A3*s*² orbitals make the major contribution to the lowest valence MO (thus, it is not a pure O2*s*² level) rather than to those MOs, which are located above the O2*s*² energy levels and are responsible for the A–L bonds. In the X-ray emission SL-spectra of sulfur compounds, the parameters of the high-intensity long-wavelength band reflecting the transition from the lowest valence MO of the complex imply that this MO is mostly S3*s*² rather than O2*s*². The data of Mössbauer spectroscopy are more difficult to interpret. The results of examination of the Mössbauer spectra (and the chemical shifts therein) of numerous compounds of antimony, tellurium, iodine, xenon do not permit unambiguous conclusions to be made on the participation of valence *Ans*² orbitals in the A–L bonds.¹⁰²

The views about a minor role of valence *Ans*² AO in the bonds with ligands are applicable to many compounds of non-transition elements of the Third and subsequent Periods but certainly, not to all of them.

Let us first consider complexes of non-transition elements of the second halves of the rows, *i.e.* Group V–VII elements: P, S, Cl, Ar (the so called late *p*-elements), and their analogues. Experimental results and general theoretical considerations based on the *ns* and *np* orbital energies and on the energies of (*np*–*ns*)-separation for free atoms A¹⁰ make it possible to draw the following significant conclusion: the valence activity of A3*s*², A4*s*², and, especially, A6*s*² orbitals is low (the inert pair effect¹⁰). For atoms of Group VII and VI non-transition elements, both the energies of (*np*–*ns*)-separation (~10–15 eV) and the ionisation potentials of *ns* and *np* orbitals are high; this rules out the donor capacity of these atoms and thus predetermines the valence inactivity of their *ns*² orbitals. In the case of the phosphorus atom and its analogues (Group V), the energies of (*np*–*ns*)-separation are no longer large (3–7 eV), but the *ns*- and *np*-orbital ionisation potentials are still high. The latter factor proves to be the crucial factor that restricts the participation of the *Ans*² orbitals in bonds with ligands.

The valence 5*s*² orbitals of antimony, tellurium, iodine and xenon atoms participate most likely in bonds with ligands. The (*np*–*ns*)-separation energies in their subgroups are the lowest.¹⁰ First of all, precise studies are needed for the electronic structures of their complexes with large coordination numbers such as [Sb(OH)₆][−], TeF₆, H₆TeO₆, IF₇, H₅IO₆, XeF₆^{2−}, [H₂XeO₆]^{2−}, *etc.* Some data on this topic have been already reported. Both the internal conversion electron spectra and XPS of Ag₆TeO₆

attest¹⁰³ to the direct participation of the Te5*s*²-electrons in the formation of bonds (whereas in TeO₂, the bonds are formed only through the 5*p*-electrons of Te). The valence XPS of Ag₆TeO₆ contains no Te5*s*²-line, which is present in the XPS of TeO₂. However, in the interpretation of the valence XPS of complexes of the Ag₆TeO₆ type, there is a risk of taking the absence of the *Ans*²-band as direct evidence for the participation of the *Ans*² orbital in the bonds with ligands, whereas this AO can be destabilised (due to changes in the valence electron density distribution or in the internal shielding) and thus, it can be masked by normal valence MOs having close energies, even though it remains a non-valence quasiatomic orbital.

Nevertheless, the actual participation of *Ans*² orbitals in the valence MOs forming the A–L bonds in some complexes seems more likely. In this case, the formation of dative (2:0) *Ans*² → L bonds or three-centre four-electron L₍₁₎ ← *Ans*² → L₍₂₎ hypervalent bonds is possible. In any case, the effective participation of valence *Ans*² orbitals in binding with ligands seems to be feasible only when a number of conditions are fulfilled. The main conditions are sufficient electron-donating capacity of the central atom A (which can be increased, for example, by the formation of primary A–L bonds involving the valence *Anp*-electrons) and large electron-accepting capacity of the ligands, up to the presence in their valence structures of vacant orbitals with low energies capable of participating in dative two-electron *Ans*² → L interactions. It is evident that high oxidation numbers and high coordination numbers of atom A are favourable for the involvement of its *Ans*² orbitals in the valence MOs.

In the case of complexes of early non-transition elements (Na, Mg, Al, Si, and their analogues), the traditional statement that their valence *Ans*¹ and *Ans*² orbitals are completely (in the majority of cases) involved in covalent bonds with ligands is beyond any doubt. These atoms are characterised by fairly low energies of the (*np*–*ns*)-separation¹⁰ and by relatively low excitation energies of valence states¹⁶

3. Occupied A2*s*² orbitals

A special position in the theory of the electronic structure of complexes of non-transition elements is occupied by elements of the Second Period. This is due to the specific spatial and energy characteristics of the valence 2*s* and 2*p* orbitals of their atoms. ‘The valence behaviour’ of the 2*s*² orbitals of atoms of the Second Period elements requires special investigation. To solve the problem of the contribution of the occupied valence 2*s*² orbitals of atoms of these elements to delocalised MOs, the X-ray photoelectron spectra of the inner atomic levels and the valence bands of nitrogen compounds with various formal valences of the nitrogen atom have been studied. Based on the results obtained, conditions of effective participation of the valence 2*s*² orbitals of the central atoms in bonds with ligands have been identified.^{104,105} The energies of the N1*s* and N2*s* levels in nitrogen compounds needed for further discussion are listed in Table 3.

Study of the effects of chemical shift of the inner 1*s* level in X-ray photoelectron spectra of nitrogen compounds demonstrates, first of all, that, in a number of its compounds, the dependence of the binding energy of the N1*s* level on the nitrogen oxidation state is nearly linear (Fig. 5). When the oxidation number of nitrogen increases by unity, the binding energy of the N1*s* level increases by ~1 eV, as has also been noticed in other studies.^{106–108} The fact that this dependence is linear implies that in these compounds, the valence 2*s*² orbitals of nitrogen atoms barely participate in the bonds with ligands (in the formation of delocalised MOs) and that the N2*s*²-electrons remain quasiatomic.⁹² The chemical bonds in nitrates, nitrites, cyanides, thiocyanates and nitrides are mainly formed from the valence 2*p*-electrons of the nitrogen atoms, the 2*s*²-electrons being inactive.

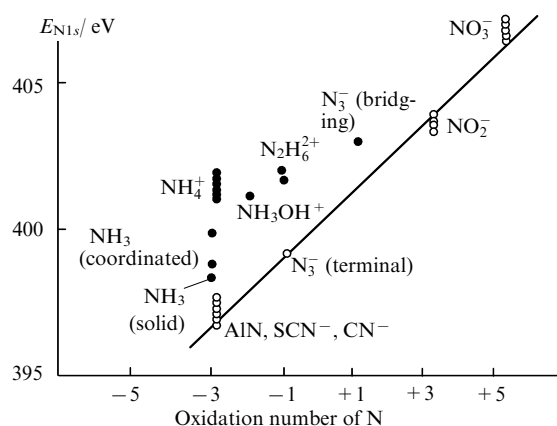
At the same time, for some lower compounds of nitrogen (NH₄⁺, N₂H₆²⁺, NH₃OH⁺), the plots for *E*_{N1*s*} deviate markedly from linearity (see Fig. 5). These deviations exceed the error in the determination of the N1*s*-energy by a factor of ten. In particular,

Table 3. Energies of inner N1s levels and valence N2s levels in nitrogen compounds.

Compound	Oxidation number of nitrogen	Energy/ eV	
		N1s	N2s
(NH ₄) ₂ SO ₄	−3	401.6	(see b)
NH ₄ H ₂ PO ₄	−3	401.6	"
NH ₄ Cl	−3	401.2	"
NH ₄ F	−3	401.5	"
NH ₄ ⁺ (see a)	−3	401.4	"
NH ₃ (coordinated)	−3	399.9	−
[Rh(NH ₃) ₆]Cl ₃	−3	398.6	−
NH ₃ (solid) ^a	−3	398.3	−
AlN	−3	397.3	22.8
Si ₃ N ₄	−3	397.4	22.8
Si ₂ N ₂ O	−3	397.2	22.6
KSCN	−3	397.7	26.3
NaSCN	−3	397.6	26.0
K ₃ [Fe(CN) ₆]	−3	397.6	26.0
N ₂ H ₄ H ₂ SO ₄	−2	401.6	(see b)
NH ₂ OH HCl	−1	401.7	"
[NH ₃ OH]Cl	−1	402.1	"
NaN ₃			
N _I , N _{III} (terminal)	−1	398.8	29.5
N _{II} (bridging)	+1	403.1	(see b)
NaNO ₂	+3	403.2	−
KNO ₂	+3	403.2	32.6
NO ₂ [−] (outer-sphere) ^a	+3	403.2	−
NO ₂ [−] (inner-sphere) ^a	+3	403.2	−
KNO ₃	+5	403.3	−
NaNO ₃	+5	407.2	35.4
LiNO ₃	+5	407.0	35.5
NO ₃ [−] (outer-sphere) ^a	+5	406.6	−
NO ₃ [−] (inner-sphere) ^a	+5	407.3	−

^a The N1s-level energies were taken from Refs 106 and 107 and scaled to the binding energy of the Cls-level, equal to 284.5 eV. ^b The N2s-level energy was not measured.

the average energy of the N1s level in the ammonium cation (401.5 eV) is much greater than that in solid ammonia (398.3 eV) or in other compounds of nitrogen with the same (−3) oxidation number. The energy of the N1s level in NH₃ is determined by the effective charge on the nitrogen atom, which appears owing to the

**Figure 5.** Energy of the N1s level as a function of the oxidation number of the nitrogen atom.

non-zero degree of ionicity of the three covalent (1:1) N–H bonds involving the unpaired 2p-electrons of the nitrogen atom and the 1s-electrons of the hydrogen atoms. The formation of an NH₄⁺ tetrahedral cation via protonation of an NH₃ molecule is possible only when the fourth N–H bond is formed by a dative mechanism (2:0), due to the transfer of electron density from the quasiatomic 2s² orbital of the nitrogen atom to the vacant 1s orbital of H⁺. Thus, the valence electron density on the nitrogen atom decreases, and its effective charge becomes positive; as a result, the inner N1s level (in NH₄⁺) is stabilised. This fact can be detected experimentally: on passing from solid ammonia (398.3 eV) to the ammonium cation (401.5 eV), the binding energy of the N1s level increases by 3.2 eV.

It is this participation of the 2s²-electrons of nitrogen in the formation of the N–H bonds in NH₄⁺ that accounts for the fact that the *E*_{N1s} value for the NH₄⁺ ion is abnormally high, taking into account the clear-cut decrease in the binding energy of the N1s level following the decrease in the oxidation number of nitrogen (from nitrates and nitrites to NH₃, nitrides, cyanides and thiocyanates), and does not fit the linear dependence. It is obvious that the same fact leads to the abnormally large chemical shifts and to the deviations from the linear dependence of the N1s binding energy on the oxidation state of nitrogen in the case of hydrazinium (N₂H₆²⁺) and hydroxylammonium (NH₃OH⁺) compounds and for the central bridging nitrogen atom in the azide anion N₃[−]. The deviation from linearity can be different in each particular case, since it depends on the type and the number of ligands bound to nitrogen, on the nature of partners of the nitrogen-containing complex in a crystal, *etc.*

Certainly, in solid ammonia, too, some participation of the 2s²-electrons of the nitrogen atom in the formation of hydrogen bonds cannot be ruled out completely; therefore, the binding energy of the N1s level in solid NH₃ exceeds somewhat the corresponding value for nitrides, thiocyanates and cyanides. The coordination of NH₃ molecules to transition metal atoms M, *i.e.* the formation of dative M ← NH₃ (2:0) σ-bonds through the 2s²-electrons of nitrogen atoms and vacant orbitals of M atoms in ammine complexes, stabilises the inner N1s levels in these complexes with respect to those in free NH₃ molecules (or in the molecules, weakly associated in the solid state). Therefore, the binding energy of the N1s level in ammine complexes is greater than that in solid NH₃; it increases as the M ← NH₃ bonds strengthens, approaching the value characteristic of the ammonium cation.

The dissimilar roles of the N2s²-electrons in the structures of N₂H₄–N₂H₅⁺, N₂H₆²⁺ and NH₂OH–[NH₃OH]⁺ can be explained by analogy with the NH₃–NH₄⁺ pair.

The deviations from linearity of the dependence of the *E*_{N1s} binding energy on the oxidation state of the nitrogen atom for some of its compounds not only indicate that the valence 2s² orbitals of nitrogen atoms participate in delocalised MOs. Besides, it can serve as additional evidence for the fact that the linearity itself in the change of the energy of the inner level of the central atom actually shows the absence of a significant contribution of the valence *ns*² AOs of atoms of non-transition elements to the chemical bonds in the corresponding complexes⁹² and the participation of only valence *np*-electrons of the central atom in the bonds with ligands. The involvement in the A–L bonds of orbitals with a different symmetry (*ns*) and with a qualitatively different spatial distribution results in sharp deviations from linearity; this is actually observed for the *E*_{N1s} binding energy in the series of nitrogen-containing compounds.

The second X-ray photoelectron criterion for the participation (or non-participation) of the 2s²-electrons of the central atom in the A–L bonds is the presence or the absence of the N2s-line in the valence XPS of nitrogen compounds and the appropriate shifting effects. In fact, the XPS of those compounds, the *Ans*-electrons of which knowingly participate in A–L bonds, contain no *Ans*-lines in the valence band (compounds of Na, Mg, *etc.*). Fig. 6 shows the valence band of the X-ray photoelectron spectra of typical nitro-

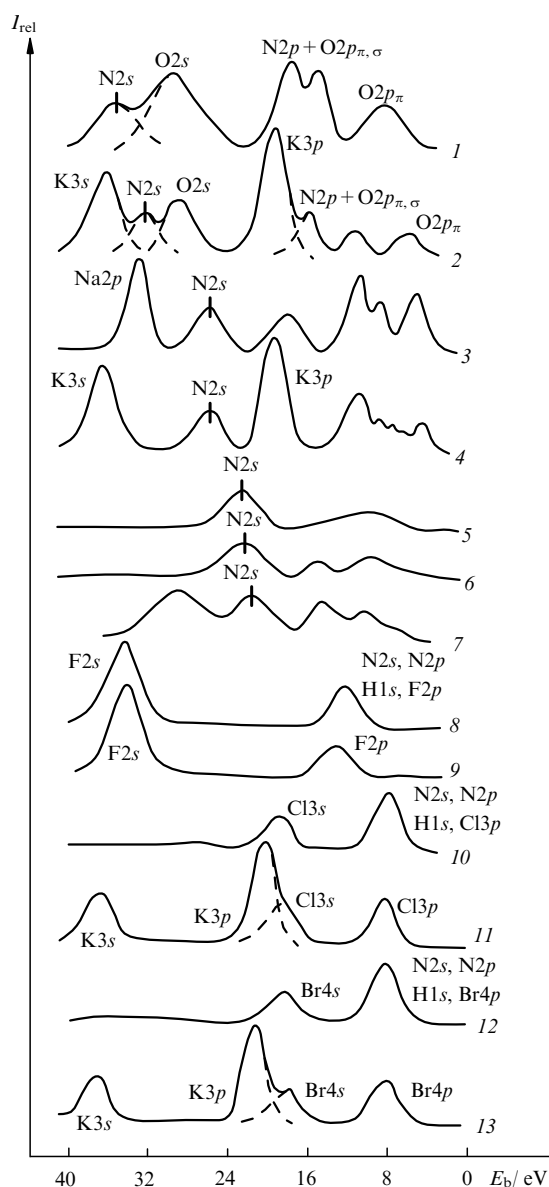


Figure 6. Valence band X-ray photoelectron spectra of nitrogen compounds.

(1) LiNO_3 , (2) KNO_3 , (3) NaSCN , (4) $\text{K}_3[\text{Fe}(\text{CN})_6]$, (5) AlN , (6) Si_3N_4 , (7) $\text{Si}_2\text{N}_2\text{O}$, (8) NH_4F , (9) LiF , (10) NH_4Cl , (11) KCl , (12) NH_4Br , (13) KBr .

gen-containing compounds: nitrates, nitrites, ammonium cations and some others. Of course, the $\text{N}2s$ -line is present in the spectra of all those compounds of nitrogen in which its valence $2s^2$ -electrons do not participate in bonds with ligands and remain quasiatomic (the binding energies of the $\text{N}1s$ level in these compounds depend linearly on the oxidation state of nitrogen, see Fig. 5). In this case, the line due to the $\text{N}2s$ level shifts regularly to lower energies as the electronegativity of the atoms bound to nitrogen decreases, *i.e.* from NO_3^- , NO_2^- to Si_3N_4 and AlN . In the NO_3^- anion, the $\text{N}2s$ level is observed at 35.4 eV, the intensity of this line in the appropriately normalised spectra of particular nitrates (LiNO_3 , KNO_3 , NH_4NO_3) being constant to within the error of determination. For these compounds, the ratio of the integrated intensities of the lines due to the $\text{N}2s$ and $\text{O}2s$ levels also remains constant. In the NO_2^- anion, the $\text{N}2s$ -level energy diminishes to 32.8 eV, and the ratio of the intensities of $\text{N}2s$ - and $\text{O}2s$ -lines increases; this is caused by the increase in the nitrogen-to-oxygen stoichiometric ratio on passing from NO_3^- (1 : 3) to

NO_2^- (1 : 2). In the spectra of silicon and aluminium nitrides and silicon oxynitride, the $\text{N}2s$ level shifts to lower binding energies to an even greater degree approaching the ionisation potential of the $2s$ orbital in the free nitrogen atom.

The main effect that is found in analysis of the valence X-ray photoelectron spectra of nitrogen-containing compounds is that the $\text{N}2s$ -line is not observed in the spectra of ammonium compounds (see Fig. 6). This fact indicates unambiguously that the $2s^2$ -electrons of the nitrogen atom are completely involved in the formation of the N-H bonds in the NH_4^+ cation. The effective participation of the nitrogen $2s$ orbitals in the valence MOs of this cation is supported by one more fact. The valence X-ray photoelectron spectra of NH_4Cl , NH_4Br and KCl , KBr , in which the positions of the $\text{Cl}3s$ - and $\text{Br}4s$ -lines remain constant, possess the following significant feature. If the spectra of NH_4Cl and KCl are normalised with respect to the $\text{Cl}3s$ -line, and the spectra of NH_4Br and KBr are normalised with respect to the $\text{Br}4s$ -line, it can be seen that the integrated intensities of the most outer bands in the spectra of ammonium compounds are markedly higher (by $\sim 30\% - 40\%$) than those for potassium compounds. This could be possible only in the case where the intensities of the outer bands in the spectra of NH_4Cl and NH_4Br contain some contribution from the molecular orbitals forming the N-H bonds and formed with participation of not only the $\text{N}2p$ - and $\text{H}1s$ -electrons with small ionisation cross-sections (91.1 and 2.7 barns, respectively), but also the $\text{N}2s^2$ -electrons with much larger ionisation cross-sections (1179 barns).¹⁰⁹

It is evident that the same reasons (the $2s^2$ -electrons of the nitrogen atom participate in the bonds in NH_4^+ and do not noticeably contribute to the bonds in NO_3^- , NO_2^- , CN^- , N_2 and NH_3) account for the difference in the forms of KVV-Auger lines of nitrogen (Fig. 7). (It should be borne in mind that here we speak about the coordinated CN^- anion, the electron structure of which differs appreciably from that of the 'free' anion; regarding the N_2 molecule, we speak mainly about the virtually non-bonding $2\sigma_u$ MO consisting mostly of the $\text{N}2s$ AO.). The valence bands in the KVV-Auger spectra of NO_3^- , NO_2^- , CN^- , N_2 and NH_3 contain two complex lines and are quite similar to one another. However, the spectrum of NH_4^+ contains only one line.¹¹⁰ Probably, these differences in the KVV-Auger spectra of nitrogen are due to the fact that its $2s^2$ orbitals participate in the bonds with ligands in NH_4^+ and are quasiatomic in NO_3^- , NO_2^- , CN^- , N_2 and NH_3 . This analogy in the

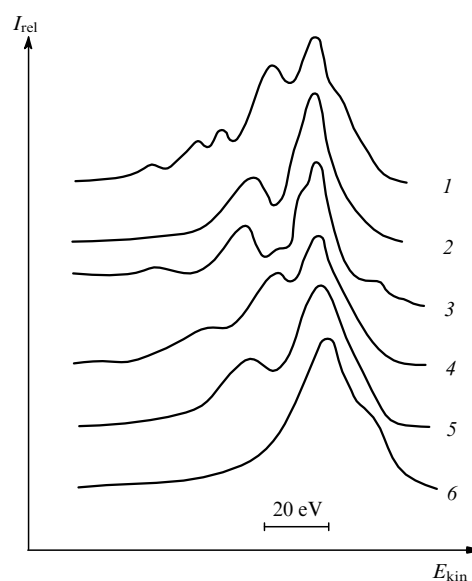


Figure 7. KVV-Auger spectra of nitrogen.

(1) NH_3 , (2) $\text{K}_4[\text{Fe}(\text{CN})_6]$, (3) N_2 , (4) NaNO_2 , (5) KNO_3 , (6) NH_4Cl , NH_4Br .

shapes of the valence X-ray photoelectron and Auger spectra of the nitrogen compounds in question is a significant argument in favour of the ideas about the electronic structures of nitrogen-containing complexes developed in this review.

We can see that the X-ray photoelectron spectra of the inner $N1s$ -electrons (the linearity in the variation of the E_{N1s} value or disturbance of the linearity) and of the valence electrons (the presence or the absence of the $N2s$ -line and shifting effects) and the KVV-Auger spectra (the presence of one or two complex bands) all indicate that the $2s^2$ orbitals of nitrogen either participate efficiently in the valence MOs, or, conversely, remain quasiautomatic in the electronic structure of nitrogen compounds. The valence XPS of those compounds for which the linear dependence of the E_{N1s} binding energy on the oxidation state of nitrogen holds, exhibit a line for the $N2s$ -electrons, and the KVV-Auger spectra of these compounds contain an additional band. The same spectra of those compounds for which the E_{N1s} values deviate markedly from the linear dependence do not exhibit the spectral bands mentioned above. The valence $2s^2$ orbitals of nitrogen in the former type of compound are scarcely involved in the A–L bonds and remain quasiautomatic, whereas those in the latter type of compound contribute considerably to the corresponding delocalised MOs.

Thus, analysis of X-ray photoelectron spectra of complexes of the Second Period elements carried out in relation to nitrogen compounds (containing nitrogen in various oxidation states) shows that the valence $2s^2$ orbitals of these atoms can both participate efficiently in the bonds with ligands and remain quasiautomatic. This depends not only on the spatial and energy parameters of the $2s^2$ AO but also on some 'indirect' parameters such as the charge of the complex ($NH_4^+ - CH_4 - BH_4^-$), the $\varepsilon_{2p} - \varepsilon_{2s}$ energy difference of the central atom, etc.

However, it is possible that the $2s^2$ AOs always participate in the formation of MOs in the complexes under consideration but the extent of this participation can be very low; therefore, it may not manifest itself in the physical properties of compounds, in particular, in the parameters of the X-ray photoelectron spectra of the valence band and inner levels. The scope of publications devoted to the results of experimental and quantum-chemical studies of the electronic structures of complexes of typical elements is immense. Therefore, it is expedient to identify the criteria for participation or non-participation of the $A2s^2$ orbitals in the A–L bonds in a general form; it is clear that these criteria will be approximate and will claim only to serve as more or less general rules.

In the majority of compounds of early typical elements (Li, Be, B, C) including diatomic homo- and heteronuclear molecules, the $A2s^1$ and $A2s^2$ orbitals, together with the $A2p^m$ orbitals, participate efficiently in typical covalent bonds with ligands, irrespective of the oxidation state of atom A, the nature of ligands L and the geometry of the complex. Both the spatial and energy factors are favourable for this participation. The main maxima of the radial density of $A2s$ orbitals are located at a larger distance from the atomic nucleus than the maxima of $A2p$ orbitals; the magnitudes of the energy of $A2s$ and $A2p$ orbitals are relatively small and are close to each other (the separation energies do not exceed 5–6 eV); the energies of excitation of valence states are also relatively low.

The electronic structures of compounds of late typical elements (N, O, F) including their diatomic molecules are much more diverse. The spatial factors are again favourable for the $A2s^2$ orbitals to be involved in the valence MOs of the A–L bonds. However, the energy factor impedes the valence activity of the $A2s^2$ AOs, since these AOs have very low energies; the fairly large energies of the $2p-2s$ separation should be taken into account (they amount to 15–20 eV, and only for nitrogen, this energy is as low as 6 eV).

In the case of atoms of late typical elements with occupied $2s^2$ orbitals, there exists, as a matter of fact, only one way for these orbitals to participate in bonds with ligands, namely, the formation of dative A–L ($2:0$) bonds. In fact, the formation of hyper-

valent $L_{(1)} \leftarrow A2s^2 \rightarrow L_{(2)}$ bonds is unlikely, due to the fairly low energies of the $A2s^2$ orbitals of nitrogen, oxygen and fluorine. Therefore, in this case, the criteria for participation of $A2s^2$ AOs in the A–L bonds go beyond the spatial and energy characteristics of $A2s^2$ AOs. For this participation, a number of conditions should be fulfilled, which are determined by the individual nature of the A and L atoms and their state in the molecule (the difference between their electronegativities, the energies of their valence orbitals, the electron populations of their AOs, etc.) An important condition for the involvement of $A2s^2$ AO in the A–L bonds is, as in the case of ns^2 AO with $n \geq 3$,⁹² the presence of a vacant acceptor orbital with a low energy in the valence structure of the ligand. In this case, the formation of a dative $A \rightarrow L$ ($2:0$) bond becomes possible even though the donor $A2s^2$ orbital itself has a low energy. A significant role is played by the electron rearrangements following the formation of the 'primary' A–L bonds involving the valence orbitals of the atom A, which leads to redistribution of the electron density in the complex. A new (with respect to the free atoms) electron density distribution gives rise to a change in the spatial and energy characteristics of the AO. These changes can be taken into account, for example, by varying the AO exponents. For $A2s$ AOs, these changes can promote an increase in the overlap with the valence orbitals of L and an approach to them in energy, i.e. they enhance the interaction of $A2s$ AOs with the ligand orbitals; however, they can also act in the opposite direction. One must bear in mind that relaxation effects (changes in the length and energy) are more pronounced for the $A2s$ AOs, which possess high penetration abilities, than for the $A2p$ AOs. Therefore, the relaxation effects caused by the formation of the 'primary' A–L bonds can result in inverted lengths of the $2s$ and $2p$ orbitals of the atom A (the $2s$ AO can become less extended than the $2p$ AO) and in increased separation energies of these AOs (i.e. substantial stabilisation of the $2s^2$ AO); consequently, the contribution of the $A2s^2$ AO to the delocalised MOs of the complex would diminish.

Apparently, for $A2s^2$ orbitals to participate efficiently in the A–L bonds, all (or most) of the above conditions need to be satisfied; each of these conditions can be regarded as necessary but not sufficient. Apparently, this accounts for the fact that in many complexes of late Second Period elements, the $A2s^2$ orbitals scarcely participate in the bonds and remain quasiautomatic.

The $A2s^2$ orbitals in the electronic structures of the molecules of hydrides FH, OH₂ and NH₃ are quasiautomatic and, according to the data of photoelectron spectra,¹¹¹ they are stabilised by 2, 4 and 7 eV, respectively, in relation to their energies in the corresponding free atoms. The role of $A2s^2$ orbitals in the valence structures of the FH_2^+ and OH_3^+ molecular cations is less obvious. The electronic structures of CH₄ and NH₄⁺ must be discussed specially; this is necessary to generalise the views about the electronic structures of tetrahedral molecules and ions, CH₄, CF₄, NH₄⁺, BH₄⁻, BF₄⁻, NR₄⁺, etc.

An important feature of the electronic structure of the NH₄⁺ cation lies in the fact that the difference between the energies of its valence molecular orbitals a_1 and t_2 is very small; according to the XPS data, this difference does not exceed 1.5–2 eV, whereas the generally accepted estimate of this value is ~10 eV (by analogy with the isoelectronic CH₄ molecule). It follows from the valence XPS of the NH₄⁺ cation (see Fig. 6) that both the a_1 and t_2 orbitals are located within the same (outer) band including also F2p, Cl3p or Br4p levels. Whereas the structure of the valence band XPS of NH₄Cl and NH₄Br, in which the Cl3s and Br4s levels are separated by 8–10 eV from the outer line, gives rise to the illusion of a large difference between the energies of the a_1 and t_2 MO in the NH₄⁺ cation, the interpretation of the valence spectrum of NH₄F does not involve any ambiguity and, therefore, it is especially representative. In this spectrum nothing is added to the outer (in energy) band (the energy of the F2s level closest to it is higher by 25 eV); both ($a_1 + t_2$) valence MOs of the NH₄⁺ cation are obviously included in this band, and this leaves no doubt in the fact that their energies are close to each other.

The energies of the a_1 and t_2 MOs of the NH_4^+ cation in the halides lie in the range of 8–12 eV and thus they are markedly higher than the energies of the $2p$ (15 eV) and, especially, the $2s$ AO (20 eV) in the free nitrogen atom. Attention is drawn to the fact that the system of 8 valence electrons is markedly destabilised on passing from NH_3 (MO: $2a_1$ — 11 eV, $1e$ — 16 eV and, especially, $\text{N}2s^2$: $1a_1$ — 28 eV) to NH_4^+ . Of course, one should bear in mind that this is a transition from a free molecule to a molecular cation in the crystal, but, nevertheless, the strong destabilisation of the $\text{N}2s^2$ -electrons on passing from the quasiatomic state (NH_3) to a delocalised multi-centre MO (NH_4^+) deserves attention.

The minor difference between the energies of the a_1 and t_2 MOs in NH_4^+ is consistent with the relatively small difference (3 eV) between the same MOs in CF_4 and differs appreciably from the corresponding value (9 eV) for the isoelectronic CH_4 molecule.¹¹² Unlike the $2s^2$ orbitals of the central atom in NH_4^+ and CF_4 participating efficiently in the valence MOs, the valence $2s^2$ -electrons of the C atom in the electronic structure of CH_4 are apparently involved only partly in the bonds with ligands and largely retain their quasiatomic character;² this predetermines the higher energy of separation of the a_1 and t_2 MOs in this case. This means that even in the ‘classical case’ of the CH_4 molecule with sp^3 -hybridisation, the problem under consideration is not simple. The $\text{C}2s^2$ -electron pair remains significantly unshared (*i.e.* the a_1 MO is non-bonding), and the C–H bonds are formed mainly due to the $\text{C}2p_\sigma$ –H1s interactions (owing to the occupation of the bonding t_2 MO); hence, the C–H bonds are orbital-deficient hypervalent bonds ($6e^-$) rather than normal covalent bonds ($8e^-$) described by equivalent MOs in terms of the sp^3 -hybridisation of AOs as in CF_4 . The above differences between the electron structures of CH_4 and CF_4 are confirmed by the fact that on passing from CH_4 to CF_4 , the average (and total) MO bonding energy increases. Undoubtedly, this relation would be the opposite if the electron structures of CF_4 and CH_4 were identical (covalent 8-electron bonds).¹⁰

Thus, in tetrahedral AL_4 molecules, the difference between the energies of valence a_1 and t_2 MOs is small in the case where the $2s^2$ -electrons of the central atom participate in A–L bonds; conversely, in the case of ‘valence inertness’ of the $2s^2$ AOs this difference proves to be fairly large. In turn, the effective interaction of the $2s^2$ AO of the central atom with the valence orbitals of ligands is largely determined by close energies of the interacting orbitals of A and L (for example, the $\text{C}2s$ and $\text{F}2p_\sigma$ orbitals in CF_4 are closer to each other than the $\text{C}2s$ and H1s orbitals in CH_4). The relationship between the energies of valence a_1 and t_2 MOs follows a complex dependence on the difference between the orbital electronegativities, on the distribution of valence electron density in AL_4 induced by the formation of the A–L bonds consisting of the $2p$ -electrons of the central atom, on the initial and optimised orbital energies of the A and L atoms depending on the effective charges on them and on some other factors. A small difference between the a_1 and t_2 MO energies may appear in both neutral molecules (CF_4 but not CH_4) and in cations (NH_4^+) and, probably, in anions as well. It can be foreseen that in the BF_4^- tetrahedral anion, the valence a_1 and t_2 MOs are characterised by a low separation energy. Indeed, the valence band XPS of BF_4^- make it possible to reliably determine this difference as being equal to ~2 eV (Fig. 8). To interpret the valence bands in the spectra of LiBF_4 and NaBF_4 , the valence band spectra of LiF and MgF_2 are also presented. The value of 2 eV is also reproduced in the DVM X_α -calculations for the electronic structure of BF_4^- .¹¹³

In the compounds of late Second Period elements, $2s^2$ orbitals of the nitrogen atoms are virtually always involved in the bonds with ligands. In this case, unlike the O and F atoms, the difference between $2p$ and $2s$ orbital energies is relatively small and close to the corresponding values for C and B. The valence activity of the $\text{N}2s^2$ orbitals depends on many factors. It is promoted by low oxidation state of nitrogen, low electronegativities of ligands, and relatively low effective charge on the N atom. These conditions are satisfied, for example, for NH_4^+ , N_2H_5^+ , $\text{N}_2\text{H}_6^{2+}$ and NH_3OH^+

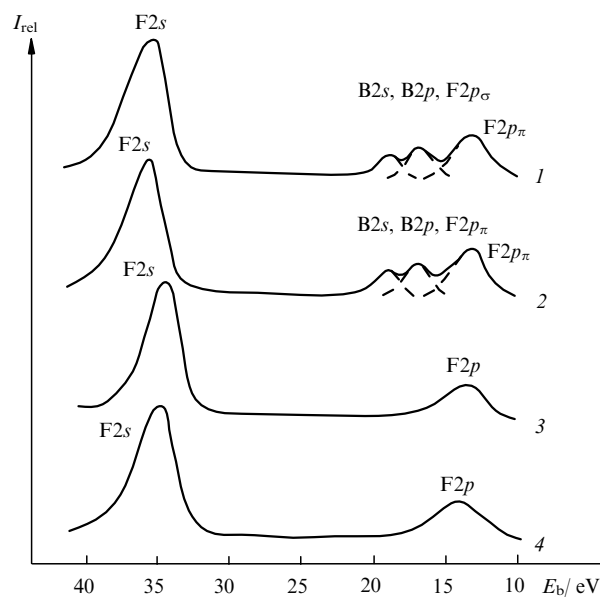


Figure 8. Valence band X-ray photoelectron spectra of the BF_4^- anion (the $\text{Na}2p$ and $\text{Mg}2p$ levels are omitted for the sake of simplicity; the $\text{Li}1s$ level lies beyond the energy range presented). (1) LiBF_4 , (2) NaBF_4 , (3) LiF , (4) MgF_2 .

cations and their substituted derivatives like NR_4^+ as well as for N_3^- and HN_3 . When some of the above conditions are not fulfilled, (for example, for NO_3^- , NO_2^- , *etc.*), the $\text{N}2s$ orbitals remain quasiatomic and markedly stabilised with respect to those in the free nitrogen atom, if they are bound to ligands with a high electronegativity. This stabilisation, observed when the unpaired $\text{N}2p$ -electrons are involved in the bonds with highly electronegative ligands, results from the decrease in the internal shielding of the $\text{N}2s^2$ orbitals, which possess a higher penetration ability than $\text{N}2p$ AOs.

In some cases, this simple picture becomes more complicated. For example, this is the case with NH_3 and NO_2^+ . In the former case, the valence inactivity of the $\text{N}2s^2$ orbital is dictated by the lack of vacancies in the valence structures of the ligands (H atoms), while in the latter case, the degree of participation of the $\text{N}2s^2$ orbital in the valence MOs is identical to the behaviour of the $\text{C}2s$ AO in the isoelectronic CO_2 molecule, which is also linear.

The very low energy of the $\text{F}2s^2$ orbital and the extremely large difference between the $2p$ - and $2s$ -energies virtually preclude the involvement of the $\text{F}2s^2$ AO in the bonds with ligands. These energy limitations diminish somewhat in the case of oxygen atoms and, therefore, participation of the $\text{O}2s^2$ orbital in bonds with ligands seems to be seldom possible. The only well-studied example illustrating this possibility is the $[\text{Ru}_2\text{OCl}_{10}]^{4-}$ and $[\text{Os}_2\text{OCl}_{10}]^{4-}$ complexes incorporating linear triatomic $\text{M} \equiv \text{O} \Rightarrow \text{M}$ groups that include ($\sigma + \pi$) two-centre double bonds and a tetravalent oxygen atom. This unusual electronic structure can easily be understood by taking into account the relaxation effects and the energetic modification of the valence AOs in these complexes following the formation of the ‘primary’ σ -bonds of the central oxygen atom with both ligands (here, a unique role is played by the two metal atoms). The formation of σ -bonds (as well as the specific environment of the M atoms in $[\text{M}_2\text{OCl}_{10}]^{4-}$) causes stabilisation of the vacant orbitals of the acceptor atoms (M) and, simultaneously, destabilisation of the two electron pairs in the valence orbitals of the donor (O); this predetermines the subsequent formation of two dative $\text{O} \rightarrow \text{M}$ π -bonds. On the whole, all the four valence orbitals of the oxygen atom including the $2s^2$ AO are involved completely in the delocalised MOs of the complex. It is possible that the $2s^2$ AO of oxygen is partially admixed with the $2p_\sigma$ AO in the electronic

structures of oxo-complexes with multiple bonds like $[\text{Ti} \equiv \text{O}]$ and $[\text{O} \equiv \text{U} \equiv \text{O}]$.

Quantum-chemical calculations for compounds of non-transition elements show¹¹⁴ that as the A–L interatomic distance increases, the contribution of the $2s^2$ AO to the MOs of the A–L bonds diminishes (probably, due to the fact that on moving away from the nucleus, the $2s$ -electron density decreases faster than the $2p$ -electron density). This has several consequences. For example, in free diatomic molecules and ions, CO , CN^- , NO^+ and some others, the $\text{A}2s^2$ AOs are often incorporated in valence MOs; when these diatomic groups are coordinated to M atoms in transition metal complexes, the multiplicity of the two-centre bonds decreases, because the electron density moves from valence d_π AO of the M atom to the antibonding π^* MO of the diatomic group; the interatomic distance in this group thus increases, and the contribution of the $\text{A}2s^2$ AO to the valence MOs probably diminishes. The same effects account for the change in the $\text{A}2s^2$ -contribution and the energy inversion of the 1π and $3(5)\sigma$ MOs in diatomic species on passing from N_2 , CO , CN^- and NO^+ with short interatomic distances to O_2 , F_2 and some other molecules with longer bond lengths.

To solve the problem of valence $2s^2$ AOs in AL_k complexes, one should take into account that the geometry of these molecules with bond angles of 104.5° need not be associated with a tetrahedral distribution of the electron density. The results of calculations carried out for H_2O not including the $2s^2$ orbital of the oxygen atom lead to a geometry similar to the experimental one, namely, the minimum total energy is achieved for a bond angle of $101-102^\circ$, without any sp^3 -hybridisation but simply due to interelectron repulsion.

To complete this section, we shall pay attention to the diversity of the electronic structures of compounds of typical elements, which defies simple systematisation (from the viewpoint of participation of the $\text{A}2s^2$ orbitals in the bonds with ligands). All the factors involved must be taken into account: the geometry of the complex, the number of atoms in it, the spatial and energy characteristics of $\text{A}2s$ and $\text{A}2p$ orbitals, the differences in the electronic characteristics of atoms A and L, etc. A representative example is the isoelectronic ($16e^-$) series of linear triatomic molecules and molecular ions: CO_2 – FCN – NO_2^+ – OCN^- – ONC^- – CN_2^- – N_3^- – N_2O . To interpret the differences between the electronic structures of these species one should take into account not only the above parameters but also some specific features characterising the properties of atoms in these systems (whether it is a central atom with a greater role of $2s^2$ orbitals or a ligand with a smaller role of $2s^2$ AOs), the total charge of the complex and some others.

The effective participation of $\text{A}2s$ AOs in the valence MOs in compounds of the Second Period elements accounts for many characteristic features of these compounds and determines the pronounced difference between the typical elements and the rest of non-transition elements, main manifestations of the Periodic Law in the chemistry of Group A elements and the biogenic character of C, N, O, etc.

VI. Principles of electronic structures of complexes of non-transition elements

Numerous results of experimental and quantum-chemical studies on complexes of non-transition elements make it possible to formulate the general principles of their electronic structure. Theoretical generalisations will always be revised, refined and improved. Therefore, we note specially that it is the X-ray photoelectron spectra (XPS) of compounds of non-transition elements that act as the paramount physical basis of our review. The studies of the intensities, energies and chemical shifts of lines in the inner-level and valence band XPS for a great number of complexes of non-transition elements with acido-ligands made it possible to observe regular repetition of consistent effects. Based on these effects, X-ray-electron criteria for the degree of participation and

the role of the valence orbitals of central atoms in the formation of the bonds with ligands were established. By analysing all the available XPS in the context of these criteria, the results of the analysis being necessarily consistent with quantum-chemical results and with the data obtained by other types of high-energy spectroscopy, the main principles of electronic structure of non-transition element complexes have been elucidated.^{104,105}

The vacant nd orbitals of the central atom A scarcely participate in the A–L bonds in the compounds under consideration, including those containing elements in the highest oxidation states, and remain virtual. Apparently, the And orbitals can contribute to the structures of the electronically excited states of complexes. It cannot be ruled out that in rare cases the And orbitals also do contribute to the ground states of complexes; this occurs when the ground state contains a considerable proportion of excited configurations.

In the electronic structures of the majority of complexes of atoms of all early (Group I–IV) non-transition elements of the Second and subsequent Periods, the Ans orbitals occupied by one or two electrons ($n \geq 2$) are involved in the valence MOs and participate in the formation of the A–L covalent bonds, together with the Anp orbitals. The electronic structures of these complexes can be described in terms of multicentre delocalised (canonical) MOs or by two-centre localised (equivalent) MOs that reflect the valence electron density distribution near the two-centre bond using the concept of hybridisation of the basis AOs. The usual views on AO hybridisation can be preserved only for coordination numbers of A atoms of no more than 4 and only for the sp^m type of hybridisation; and even in this case, this should be done with a certain caution (cf. CH_4 and CF_4).

The occupied Ans^2 orbitals ($n \geq 3$) of the atoms of late (Group V–VIII) non-transition elements of the Third and subsequent Periods make a fairly small contribution to the valence MOs of most of the complexes. In the case of ligands with high electronegativities, the valence Ans^2 orbitals remain quasiatomic and markedly stabilised (with respect to those in the corresponding free atoms A). The contributions of Ans^2 orbitals to delocalised MOs are appreciable in some complexes with large coordination numbers (for instance, $\text{Te}5s^2$ in Ag_6TeO_6).

The A–L bonds in most complexes of late non-transition elements of the Third and subsequent Periods, unlike those in the analogous compounds of transition metals, are formed with participation of only valence np orbitals of central atoms (in contrast to the traditional views stating that the ns , np and nd AOs participate in bonds irrespective of their electron populations in the free non-excited atoms A). Here, the concept of hybridisation of the basis AOs is irrelevant. It is expedient to describe the electronic structures of these acido-complexes in terms of MOs containing no contribution of the And and Ans^2 orbitals and consisting of only the Anp^m (and, in some rare circumstances, Ans^2) orbitals and in terms of covalent and hypervalent A–L bonds. To describe these complexes within the framework of the general MO LCAO theory, the hypervalent structure is the best approximation. Generally, the chemistry of phosphorus, sulfur, chlorine, argon and their analogs can be regarded as the chemistry of compounds, the electronic structures of which are built mainly from valence np^m orbitals of the central atom and hardly contain any contribution of the Ans^2 and And orbitals to the valence delocalised MOs.

In the complexes of late elements of the Second Period (N, O, F), the main and sometimes the only contribution to the MOs is made by the valence $\text{A}2p^m$ orbitals. In some complexes, the occupied $\text{A}2s^2$ orbitals prove to be valence inactive and remain quasiatomic, while in some other complexes, they participate efficiently in the formation of delocalised MOs. The involvement of the $2s^2$ -electrons of central atoms (and sometimes, the ns^2 -electrons with $n \geq 3$) in the bonds with ligands is possible only when a number of conditions are satisfied; the most important condition is the presence of a low-energy vacant orbital (i.e. a strong acceptor AO) in the valence structure of the ligand. The

two-centre A–L bonds consisting of the $A2p^m$ -electrons are formed both by the covalent (1 : 1) and the dative (2 : 0) mechanisms, and those consisting of the $A2s^2$ -electrons are formed, as a rule, by the dative mechanism.

In the electronic structures of complexes of the Second Period elements, covalent and hypervalent π -bonds are often formed, due to the $A2p_\pi$ -electrons.^{115–117} The simultaneous participation of $A2s$ AO (together with $A2p$ AO) in the A–L σ -bonds leads to the formation of high-multiplicity homo- and hetero-atomic two-centre bonds ($N\equiv N$, $[C\equiv N^-]$, $C\equiv O$, etc.). For $n \geq 3$, the possibility of the formation of covalent and, especially, hypervalent π -bonds upon the interaction of Anp_π orbitals is sharply decreased; therefore, the electronic structures of complexes of non-transition elements of the Third and later Periods seldom contain multiple two-centre bonds.^{3,45}

In conclusion, let us discuss the theoretical substantiation of the principles formulated above. The primary attention will be focused on two factors, viz. the energy and spatial factors.¹⁰⁴

The theoretical justification of the valence inactivity of vacant nd and occupied ns^2 orbitals ($n \geq 3$) of the central atoms in the electronic structure of complexes of non-transition elements of the Third and subsequent Periods is based on the fact that the energy difference between these AOs, on the one hand, and the valence orbitals of the ligands, on the other hand, is great. The energies of the vacant nd orbitals are too high and those of the occupied ns^2 orbitals are too low compared to the energies of the valence orbitals of the acido-ligands, which have higher electronegativities than atom A (the energies of Anp orbitals are close to the energies of σ, π orbitals of the ligands). The large difference between the orbital energies is reinforced by the fact that the And orbitals are fairly diffuse and the Ans^2 AOs are strongly contracted; this also hampers their effective interaction with ligand orbitals (the length of the Anp AO is the optimum in this respect). Hence, the participation of vacant And and occupied Ans^2 orbitals in the MOs of bonds with typical ligands is hampered by both the energy and spatial factors.

The theoretical substantiation of the participation of the occupied valence $A2s^2$ orbitals of the Second Period atoms in the molecular orbitals of complexes with acido-ligands is mainly based on the fact that their $A2s$ AOs are more extended in space than the $A2p$ AOs (the main maxima of the radial density of the $A2s$ AOs are located farther from the nucleus than those of the $A2p$ orbitals). For the rest of the valence AOs with $n \geq 3$, the situation is known to be the opposite, and this accounts for the fact that $A2s^2$ AOs participate in A–L bonds far more efficiently than any other ns AO. Thus, in this case, the crucial role belongs to the spatial factor, which ensures a high value of the numerator (via the overlap integral) in the expression for the energy of stabilisation of a bonding MO [see formula (1)]. It is owing to their specific spatial characteristics that the $2s$ AOs of atoms A, unlike ns AOs with $n \geq 3$, often participate efficiently in the formation of delocalised MOs. The crucial role of the spatial factor,¹⁰⁴ which ensures that the magnitudes of the overlap integral for the interaction of the $2s$ orbitals of atom A with the valence orbitals of ligands are larger than those for all the other ns orbitals, is stressed by the fact that the contribution of the occupied $A2s^2$ orbitals to the valence MOs diminishes with increase in the A–L interatomic distances,¹¹⁴ and also by the fact that the energy factor exerts a restraining influence on the participation of occupied $A2s^2$ AO in the A–L bonds (in fact, the $2s$ AO energies are much smaller than the energies of valence orbitals of the ligands; therefore, the denominator in the equation mentioned above is always large). However, the energies of $A2s$ (generally, Ans) orbitals may come closer to those of the valence orbitals of ligands, as a result of redistribution of the valence electron density in the complex, caused by the formation of ‘primary’ A–L bonds from the valence $A2p$ (or Anp) orbitals, i.e. due to electron rearrangements controlled by the differences in the atomic characteristics of A and L. However, the same electron rearrangements

can also cause the opposite effect, namely, a decrease in the spatial dimensions of ns AOs and in their energies, i.e. their energy discrepancy with the valence orbitals of ligands can thus be aggravated.

VII. Conclusion

To avoid unfavourable criticism of theorists engaged in the theory of electronic structures of complexes of non-transition elements or of those going to work in this field in the future, we should like to emphasise that our review deals with the main principles of the electronic structures of complexes of non-transition elements.

Certainly, the quantum nature of electrons gives rise to the tendency for their delocalisation. Therefore within the framework of the MO LCAO formalism, which is a part of the wave mechanics of atoms and molecules, it is always possible and even likely that non-zero contributions to the electron density in the electronic structure of a molecular system are made by those states which remain vacant in free unexcited atoms. This refers, in particular, to the And orbitals in non-transition element complexes. However, while describing the electronic structure of these systems, one must not lose the sense of proportion required in any situation (the speculations on the problem of d orbitals in many papers, reviews and monographs in which too much attention is paid to details, while the main meaning is lost, suffer from the lack of this sense). The more so, because views on the atomic s , p and d orbitals in a molecule are not rigorous. The angular momentum of electrons is not conserved in molecules, and the classification of states as s -, p -, and d -types loses its meaning. Only near the atomic nucleus, is there a region where the influence of the molecular environment is fairly minor compared to the nuclear field, so that the concept of s , p and d orbitals is roughly retained. Therefore, by the participation of And orbitals in the A–L bonds, we mean the presence of occupied single-electron states that have the form of d orbitals near the nucleus of the central atom A and are modified away from the nucleus, in conformity with the influence of the molecular environment.¹¹⁸

It is precisely and solely in this sense that we proclaim the general idea on the valence inactivity of And orbitals in the electronic structure of non-transition element complexes and on the valence activity of Ans^2 orbitals being markedly lower than is usually assumed.

In this review we express our opinion: the role of And orbitals in the majority of cases is negligibly small. These orbitals are so unfavourable in energy and so diffuse that they are incapable of any substantial interaction with the valence orbitals of the ligands. In *ab initio* calculations, d orbitals are important as polarisation functions but their population is much smaller than has been assumed in the $sp^m d^n$ -hybridisation model.

Some recent publications devoted to the electronic structures of non-transition element complexes present the results of theoretical studies of several complexes of this type carried out using empirical methods,^{119–120} density functional¹²¹ and other high-level quantum-chemical calculations.^{122–125} The results of these studies are not inconsistent with the main (conceptual) conclusions made in our review.

However, the foregoing refers to the ground states of complexes. In the excited states, the participation of d AO in bonds and their influence on the molecular properties can be markedly higher than those in the ground state. However, up to now, no reliable calculations on the excited states of complexes as applied to the problem of d AOs have been reported. It has been shown¹²⁶ that the participation of the d orbitals of the central atom in MOs can result from the interaction of a non-excited configuration containing no d -contribution with electron-excited configurations having fairly occupied d orbitals.

In this connection, it seems necessary to consider briefly the X-ray diffraction studies dealing with the electron density distribution in crystals. Precision calculations based on these experi-

ments provide reliable data, convenient for further processing, on the differential and deformation electron densities, the ease of dealing with these results has withstood the test of time better than many complicated constructs and refined approaches. The theoretical interpretation of the results obtained recently along this line point to the substantial electron population of *And* orbitals. At present, there are only few results of this type, but they are attracting considerable attention and require a clear and strict explanation.

The direct proof for the population of the $Si3d$ orbitals in the SiO_4^{4-} anion is among the first examples of this sort.^{127,128} The distribution of the differential ($\Delta\rho$) and total (observed experimentally, ρ^0) electron density in the crystal of γ - Ni_2SiO_4 has been studied quantitatively based on the set of measured structural amplitudes;¹²⁷ in this study, a substantial electron population of the $Si3d$ orbitals in the tetrahedral SiO_4^{4-} anion and their strong compression were found (the experimental effective charge on the Si atom amounts to +2.5). We believe that if the electron density in the $Si3d$ orbitals of γ - Ni_2SiO_4 is actually fairly high, this can apparently be explained in the following way. A large contribution to the real state of SiO_4^{4-} in the γ - Ni_2SiO_4 crystal is made, in addition to the non-excited configuration of the free hypothetical SiO_4^{4-} anion, by its electronically excited configurations, which can contain a considerable proportion of the $Si3d$ orbitals. The large contribution of the electronically excited configurations can be due to the 'extreme' environment of the SiO_4^{4-} anion in the crystal of γ - Ni_2SiO_4 consisting of several Ni atoms with high positive charges (+1.3). It is significant that the electronic structure of the SiO_4 -group in the SiO_2 crystal rules out the participation of the $Si3d$ functions in the valence orbitals. This has been found¹²⁹ in a study of photoionisation, X-ray emission ($SiK\beta$, $SiL_{2,3}$, $OK\alpha$) and ultraviolet excitation of SiO_2 ¹²⁹ and in SCF SW X_α -calculations of the electronic structure of the SiO_4 -group in SiO_2 . The environment of the SiO_4 -groups in crystalline quartz has nothing in common with that in γ - Ni_2SiO_4 ; in SiO_2 , they can be isolated only as $SiO_{4/2}$, which assumes that the SiO_4 -group is surrounded by Si atoms with fairly small charges. There are no indications of any substantial contribution of the $Si3d$ orbitals to the electronic structure of Na_2SiO_3 . It has been noted¹²⁸ that on the cross-sections of deformation densities of $AlPO_4$ and $CaSO_4$ crystals, some peaks can be observed that correspond to the partly occupied $3d$ orbitals of phosphorus and sulfur atoms in the PO_4^{3-} and SO_4^{2-} anions, isoelectronic with SiO_4^{4-} .

One of the complications in solving the problem of *And* orbitals lies in the multielectron character of the wave function of the molecule. Therefore, it is necessary to distinguish between the influence of *And* AOs on the properties of a molecular system and manifestation of *And* AOs in a direct study of the electron density or in calculations of the electronic structure of a molecule by multiconfiguration methods of quantum chemistry.

Thus, there are grounds to believe that, under certain conditions, appreciable electron population of *And* orbitals in non-transition element complexes is quite possible and is largely promoted, among other factors, by a great contribution of electronically excited configurations to the wave function of a complex. It can be assumed that substantial *And*-electron populations are typical of many short-lived electronically excited states of the complexes under discussion (the contribution of electronically excited configurations to these states is great by definition) as well as some (apparently, relatively rare) stable states of complexes in which, due to certain reasons, the contribution of electronically excited configurations is large.

So, both empirical concepts — the concept of *d* orbitals and hypervalent bonds — although they seem attractive due to their simplicity and apparent versatility, cannot serve any longer for the strict description of the electronic structures of complexes of non-transition elements; in principle, the latter concept is certainly a better approximation. In both concepts, an important role, although non-equivalent, in the formation of bonds with ligands

is attributed to the valence ns^2 orbitals of the central atom A, and this point is their common flaw (recall that even in the concept of hypervalent bonds, which is the best approximation for the description of the electronic structures of the complexes in question, the participation of valence ns^2 -electrons of central atom A in binding with ligands is assumed for higher compounds in which the oxidation state of A is maximum). The ideas about hybridisation of valence orbitals of the central atom, including isovalent hybridisation, (not increasing the valence), are applicable only to complexes of elements of the Second Period. In this case, they are fairly effective (with the exception of molecular compounds of fluorine and oxygen), because the energy and spatial characteristics of valence $2s$ and $2p$ orbitals give the best fit to each other.^{45,104}

The theory of the electronic structure of non-transition element complexes has not yet been completed. Some of its points require refinement and reasoned modification. There are also blank spots in it, which account for the necessity for the formation and development of conceptually new ideas: for example, in connection with the electronic structure of so-called double bonds: S—O in H_2SO_4 , P—O in H_3PO_4 , the multiplicity of which is actually much less than two.⁴⁵ Of course, the main point is the problem of valence of central atoms and the adjoining problem of the instability of PH_5 , SH_4 , SH_6 , etc. The existing views stating that SO_3 , H_2SO_4 and SF_6 contain hexavalent sulfur and P_2O_5 , H_3PO_4 and PF_5 contain pentavalent phosphorus seem to be no more than a myth, which is simple and convenient for a non-theorist chemist but, in many respects, delays the progress of the theory.

The fact (more precisely, the paramount sign) that in the majority of non-transition element complexes, only *p* AO of the central atom participate in the 'central atom—ligand' orbital interactions accounts for the sharp differences between the electronic structures of complexes of non-transition elements and transition metal complexes. In the electronic structure of the latter, both spatial and energy factors are often favourable for efficient participation of all types of valence orbitals of the M atom [ns , $(n-1)d$, np] in delocalised MOs, in conformity with the symmetry of the complex. This, in turn, explains easily and simply, why transition metal complexes are characterised by more diverse bond multiplicities and also by greater valencies of central atoms M than the corresponding non-transition element complexes, and also why the former are generally more stable.

However, apparently, the electronic structure of transition metal complexes is also far from this ideal scheme; this is indicated by the results of recent investigations on the roles of various valence orbitals in the chemical bonding in ML_k complexes. Based on the calculated¹³⁰ wave functions for $Ni(CO)_4$ and $Cr(NO)_4$, the structure of the 'central atom—ligand' bonds has been analysed within the framework of a new method, free from the artifacts of the traditional analysis of electron populations. It was shown that it is the $3d$ orbitals of atoms M ($3d$ -Ni, $3d$ -Cr) that make the predominant contribution (apart from the ligand orbitals) to the covalent M—L interactions, whereas the contribution of $4s$ and $4p$ AOs is negligibly small.

Although the above results are not general (only two complexes were studied), the main conclusion can be regarded as the beginning of a concept assuming a crucial role of valence $(n-1)d$ orbitals of atoms M in M—L bonds and, simultaneously, valence inactivity (more precisely, low valence activity) of their ns and, especially, np orbitals in the electronic structure of transition metal complexes ML_k . Together with the general conclusion about the crucial role of valence np orbitals of central atoms A in A—L bonds in complexes of non-transition elements and about the valence inactivity of their ns and, especially, nd orbitals, this can lead to a nontrivial and a very simple view on the most general principles governing the electronic structure of the two 'polar' types of complex, AL_k and ML_k , namely: transition metal complexes are mostly formed due to the valence *d*-electrons of central

atoms, whereas complexes of non-transition elements are formed from the valence *p*-electrons of central atoms.

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Self-organising structures of lecithin

Yu A Shchipunov

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Abstract. Modern concepts of the self-assembly of amphiphiles are considered on the example of self-organising structures of the natural lecithin. Binary, ternary and multicomponent systems are discussed. A considerable part of the review is devoted to the peculiarities of self-organisation of this phospholipid in non-aqueous media and to the role of polar organic solvents. Virtually all of the structures formed by lecithin are examined: micelles, swollen micelles, microemulsions, emulsions, organogels, vesicles (liposomes), and lyotropic liquid crystals. In each specific case, attention is drawn to the dependence of self-assembly at the macroscopic level on interactions at the molecular level, shape of molecules, and their solvation and packing at the interface. The self-organising lecithin structures formed in the interfacial area of immiscible liquids in the course of unrestricted adsorption from the bulk of non-aqueous solution are considered. The bibliography includes 282 references.

I. Introduction

The term 'self-organising structures' has appeared in physical and colloid chemistry rather recently. It was borrowed from molecular biology where it serves to describe the mode of cellular structure assembly from constituent molecules. Nowadays, much attention is being given to the elucidation of principles and mechanisms underlying the aggregation of substances and their association into supramolecular systems.

Lecithin is the best known of all natural surfactants. It is widely distributed in living nature, being a basic structural component of the lipid matrix of biological membranes and membranous organelles, and finds uses in food industries, cosmetics, pharmacology, and biotechnology as an effective dispersive and emulsifying agent. All this explains the keen interest of investigators from different fields of science in studies of lecithin properties, its self-organisation, the structures formed, and their transformation.

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Lecithin forms monomolecular layers, bimolecular films, liposomes and vesicles, liquid crystals, emulsions and microemulsions, and organogels. The systematic studies, which are underway in many laboratories virtually through all this century, have provided a tremendous body of experimental material on its structural organisation in various media. Numerous monographs and reviews devoted to phospholipids and surfactants describe the specific properties and phase behaviour of lecithin; however, no generalising consideration and analysis of its self-organisation have been done until now. The present review is an attempt to fill in this gap.

II. Composition of the lecithin molecule

Lecithin belongs to the class of phospholipids. The content of phospholipids in living cells varies from 15 mass % to 50 mass % (dry mass), whereas in the nerve tissue its level is as high as 60 mass %–80 mass %.^{1–4} Lecithin dominates over other phospholipids in marine invertebrates, plants, and animals.^{1–5} In animal organs and tissues, lecithin is mostly contained in the nerve tissue, liver, heart, lungs and blood.^{2,4} The content of lecithin often exceeds that of any individual phospholipid.^{1–5}

The principal natural sources of lecithin are egg yolk and soybeans. The yolk accounts for 30%–35% of the egg mass of which ~1/3 is lecithin.⁴ The content of phospholipids in the soybean oil is much lower ranging from 1.5% to 2.5%. Nonetheless, soybeans are the major industrial source of lecithin. The soybean lecithin accounts for as much as ~90% of the annual world lecithin production of 145 000 tons.⁶ This is explained by the large scale of soybean oil production. For example, 16 m tons of this oil was produced in 1989–1990.⁴ Accordingly, the phospholipids, which are obtained as by-products in the soybean oil purification, accounted for about 300 000 tons of which 40% was lecithin.⁴

Lecithin is an ester of glycerol in which two hydroxy groups at positions 1 and 2 are esterified by higher fatty acids, whereas the third hydroxyl is esterified by phosphoric acid to which a choline residue is attached (Fig. 1). Owing to the presence of phosphate residue, phospholipids are sometimes called 'phosphatides', while lecithin is widely known as 'phosphatidylcholine'.

The fatty acid composition of the egg yolk and soybean lecithins is presented in Table 1. It is seen that the latter is more unsaturated. Usually, a saturated fatty acid residue is at the position 1, while the residue of an unsaturated acid occupies the position 2.⁸ In its physicochemical properties, the egg yolk lecithin is close to 1-palmitoyl-2-oleyl-*sn*-glycero-3-phosphatidylcholine⁹

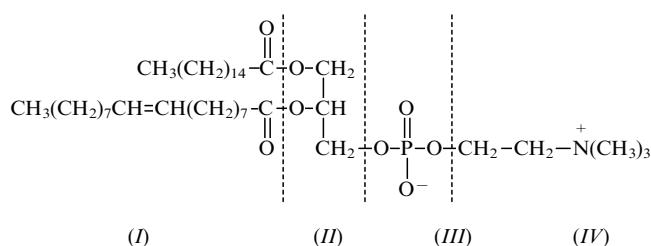


Figure 1. The structural formula of 1-palmitoyl-2-*sn*-glycero-3-phosphatidylcholine, an analogue of egg-yolk lecithin. (I) fatty acid residues; (II) glycerol residue; (III) phosphate group; (IV) choline.

(Fig. 1). No close synthetic analogues of the soybean lecithin have been suggested to date.

Table 1. Fatty acid composition of natural lecithins.

Fatty acid composition						Molecular mass	Ref.
C _{16:0}	C _{16:1}	C _{18:0}	C _{18:1}	C _{18:2}	C _{18:3}		
Soybean lecithin							
12.2	0.4	2.7	10.7	67.2	6.0	773	10
Egg lecithin							
35.8	1.5	18.3	37.4	6.8	—	766	11

One should pay attention to the following important fact. The fatty acid composition of natural phospholipids is heterogeneous (Table 1); however, it does not exhibit any substantial variation from sample to sample and is little dependent on the lecithin source. An important consequence is that all investigators deal with natural phospholipids, which are sufficiently close by their composition. This allows an adequate comparison of the results obtained at different times and in different laboratories.

III. The factors determining self-organisation

The lecithin molecule carries two non-polar hydrocarbon chains and a voluminous polar region composed of residues of three molecules (Fig. 1). The lecithin molecule is neutral in the pH range of 3–12.⁷ The combination of two large moieties of opposite polarities occurs definite effects on all the physicochemical properties of lecithin. For instance, it cannot exist in the molecular form in media of any polarity.^{12, 13} Lecithin is either concentrated at the interface or self-assembled into micelles or liquid crystals in the bulk solution.

1. Hydrophobic effects

The existence of two hydrocarbon chains drives the lecithin molecule out of the water towards the interface or stimulates its association with other molecules. In aqueous solution, these chains are surrounded by water molecules which, owing to additional hydrogen bonds, are less mobile and more structured than the bulk-distributed solvent molecules. Therefore, the dissolution of non-polar compounds leads to an entropy (*S*) decrease, which proves to be rather significant. Being of entropic nature, this effect is known as ‘hydrophobic’.¹⁴ The resulting change in the free energy may be expressed as

$$\Delta G = \Delta H - T \Delta S, \quad (1)$$

where *H* is the enthalpy, and *T* is the temperature. Changes in the standard free energy upon transition from aqueous solution to oil may be estimated using the equation, proposed^{15–17} for the calculation of the hydrophobic effects in the adsorption of surfactants

$$\Delta G_a^\circ = -C_a(38.3n_{\text{CH}_3} + 31.9n_{\text{CH}_2} + 18.6n_{\text{CH}} + 1.9n_{\text{C}}), \quad (2)$$

where *C_a* is the adsorption coefficient equal to 106 J mol^{−1} Å^{−2}, *n* is the number of the respective hydrocarbon groups, the factors involving *n* are the areas of the cavity surface (in Å²) formed around the group indicated by the subscript. According to Eqn (2), the absolute value of ΔG_a° for the lecithin molecule containing the hydrocarbon chains of 15–17 carbon atoms can be higher than 100 kJ mol^{−1}.

2. Thermodynamic description of self-organisation

The contact of hydrocarbon chains with water can also be excluded by the aggregation of amphiphilic molecules. This may result in the formation of various structures. Their common feature is that the surface is covered by polar groups shielding the inner volume filled with non-polar groups. Micelles are the best known example. As a matter of fact, the thermodynamic description of the self-organisation is based on the approach[†] proposed for micelle formation by Tanford¹⁹ and supplemented with molecular geometry by Israelachvili *et al.*^{20, 21} that permitted its application for any self-organising structures.

Let us represent the process of aggregation of one type non-ionogenic surfactant in the form of a reversible chemical reaction



where *B* and *M* stand for the surfactant molecule and micelle, respectively; *N* is the aggregation number. The condition of aggregative equilibrium in a micellar system coincides with the condition of equilibrium of a reversible chemical reaction that was first deduced by Gibbs^{18, 22}

$$N\mu_1 = \mu_N, \quad (3)$$

where μ_1 and μ_N are the chemical potentials of a compound in the monomeric and aggregated states, respectively. Taking into account the expression for the chemical potential

$$\mu = \mu^\circ + RT \ln X,$$

one may transform Eqn (3) into

$$N\mu_1^\circ + NRT \ln X_1 = \mu_N^\circ + RT \ln X_N, \quad (4)$$

where μ_1° and μ_N° are the standard chemical potentials of a compound in the monomeric and aggregated states, respectively; *X*₁ and *X_N* are the mole fractions of this compound in each state, *R* is the gas constant, and *T* is temperature. The equation does not include the activity coefficients, since the interactions between non-aggregated molecules and between aggregates were not considered.

In this case Eqn (4) at *N* → ∞ gives an approximated equation

$$\Delta G_N^\circ = -A_N^\circ \simeq RT \ln X_{\text{CMC}}, \quad (5)$$

where ΔG_N° is the change of the standard free energy during the aggregation of surfactant, *A_N*[°] is the standard affinity for micellisation,[‡] *X_{CMC}* is the critical concentration of micelle formation.

In colloidal chemistry, Eqn (5) is often used to calculate the standard free energy of micelle formation.^{14, 18, 23} The critical micelle concentration is easily found from the experimental property — composition dependence of surfactant solutions. In the scale of molar fractions, the standard substance concentration is assumed to be unity.¹⁸

One can estimate the magnitude of ΔG_N° for dipalmitoyllecithin. For this phospholipid, the critical micelle concentration in water is 4.6×10^{-10} M.²⁴ Substitution of this value into Eqn (11)

[†] It should be noted that the approach to the description of micelle formation is not uniform. To this end, various models were proposed in the literature. They are exhaustively discussed in the substantial monograph by Rusanov.¹⁸ The present review provides a schematic account of the basic concepts of the thermodynamics of micellisation.

[‡] The affinity for micellisation corresponds to the chemical affinity for reaction in thermodynamics (for details, see Ref. 18).

gives the standard free energy of micelle formation of 53 kJ mol^{-1} (at 25°C). In order of magnitude, this value is comparable with the standard free energy of adsorption.^{16, 17}

If the dependence of ΔG_N° on temperature and pressure (p) has been established (for which purpose experimental values of CMC under different conditions are required), it is possible to calculate the volume-related (V_N°) effects accompanying micellisation and the standard thermodynamic functions of aggregation, *i.e.* entropy (S_N°) and enthalpy (H_N°).

Analysis of the standard thermodynamic functions alone does not permit the estimation of the aggregate size or the prediction of the type of the structures formed. Therefore, the description of the processes underlying the self-organisation of amphiphiles usually includes the consideration of intermolecular interactions.^{14, 18, 20, 21, 25–28} In the standard free energy of aggregation, two groups of components are distinguished: standard energies of attractive and repulsive interactions. A balance of these interactions determines the optimal packing of amphiphilic molecules, which in turn defines the type of self-organising structures.

3. The dimensionless packing parameter

It has been proposed^{20, 21, 25} to characterise the packing of amphiphilic molecules in aggregates by three parameters: the optimal area A_0 occupied by one molecule at the interface, the volume V of hydrocarbon chains, and the maximal length $L_{\max}$ to which the chains are extended in the *trans*–*trans*-conformation. Criteria of such packing are derived from the following consideration.

The aggregation number, *e.g.* spherical, of micelles with radius r may be expressed as

$$N = 4\pi \frac{r^3}{3V}. \quad (6)$$

It is assumed^{18, 20, 21, 25} that the molecules are incompressible, and that the radius of spherical aggregates cannot be larger than $L_{\max}$. In this case,

$$r = 3 \frac{V}{A_0} \leq L_{\max}. \quad (7)$$

This allows transformation of Eqn (7) into

$$N = 4\pi \frac{r^2}{A_0}. \quad (8)$$

The criterion of amphiphile micellisation is derived from Eqn (8). Provided that the above-stated conditions are met, the molecules whose size satisfies the requirement

$$S_p = \frac{V}{A_0 L_{\max}} \leq \frac{1}{3}, \quad (9)$$

will organise themselves into spherical aggregates.

The criteria of all other types of structures (Fig. 2) are established in a similar way.

The criterion S_p is commonly called ‘the dimensionless packing parameter’, since the $V/(A_0 L_{\max})$ ratio is dimensionless. This term will be used further in this review.

Numerous studies^{20, 21, 25–30} showed that the consideration of molecular geometry alone makes it possible to predict the character of the structural organisation of amphiphiles. In a number of instances, the theoretical aggregation number and micelle size are in good quantitative agreement with the experimental values. Nonetheless, the estimation of the magnitude of the dimensionless packing parameter is far from being simple. The major difficulties are related to the determination of real A_0 and $L_{\max}$ values. Calculations based on molecular models give an S_p parameter which differs markedly from its real value.³¹ This discrepancy is due to the fact that the amphiphile structures are not in the molecular form but in the solvated state. The solvation shell imposes definite steric constraints on the packing of molecules.

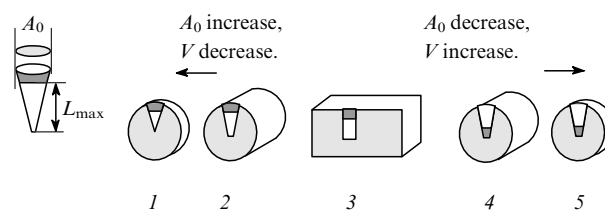


Figure 2. Types of structures formed by amphiphiles and the corresponding values of the dimensionless packing parameter S_p : (1) $1/3$ (micelles); (2) $1/2$ (hexagonal structures); (3) 1 (lamellar structures); (4) 2 (inverted hexagonal structures); (5) 3 (reverse micelles).

Accordingly, these should be accounted for in the parameters V , A_0 , and $L_{\max}$. In order to make realistic estimates, one should know the number of solvent molecules in the solvation shell as well as its structure.^{31–33}

Nowadays, the parameter S_p is used basically for qualitative estimates. Based on simple geometric concepts, the use of the dimensionless packing parameter permits prediction of the type of self-organising structures and the direction of phase transformations. The effects of compounds on the structure of amphiphiles are interpreted with due account for their additivity.^{29, 30, 34} In other words, the use of S_p makes it possible to approach the development of a system with the required structural organisation without resort to complex, arduous, and time-consuming studies (see, for example, Ref. 35).

IV. Binary systems

1. Lecithin–water

Natural lecithins in their molecular form are virtually insoluble in water (the solubility is of the order of 10^{-10} M).¹² Nevertheless, they are hygroscopic. Sometimes, even azeotropic distillation with benzene lasting many days fails to remove water completely. Therefore, lecithins, even after thorough drying, usually contain ~ 1 molecule H_2O per phospholipid molecule.¹⁰ Lecithin is insoluble in aqueous solutions, but rather swells. Depending on the magnitude of water/lecithin ratio, various liquid-crystalline structures are formed. This property has been given the name of ‘lyotropic mesomorphism’.

a. Liquid crystals

Binary phase diagrams of egg lecithin–water and soybean lecithin–water systems are presented in Fig. 3. Their superposition shows that the diagrams are not fully analogous, which is due to the difference in the fatty acid composition of two lecithins.

The lamellar liquid-crystalline mesophase L_α [§] is predominant in lecithin–water mixtures. It is formed by numerous parallel lamellae arranged into a bimolecular layer (Fig. 3). The polar groups of phospholipid molecules are localised on the bilayer surface, while their hydrocarbon chains fill the inner volume. Water molecules form a hydration shell around the polar groups and an aqueous interlayer between lamellae.

At room temperature, a homogenous lamellar liquid-crystalline mesophase L_α exists when the water content is in the range from 9 mass %–10 mass % to 43 mass %–45 mass % for egg lecithin and from 7 mass % to 35 mass % for soybean lecithin. In sealed tubes, the mesophase L_α is preserved up to 220 – 240°C . At higher temperatures, it melts to form an isotropic liquid composed apparently of reversed micelles (L_2 phase). When the water content exceeds the indicated limits, the lamellar mesophase L_α separates into the mesophase L_α and aqueous solution. This is the region of liposome and vesicle formation.

At low water levels (< 10 mass %), the formation of other liquid-crystalline mesophases is observed: lamellar L_β , hexagonal H_{II} , and cubic Q_x (Fig. 3). Note that the non-bilayer mesophases

[§] Liquid-crystalline mesophases are designated according to Luzzati.³⁶

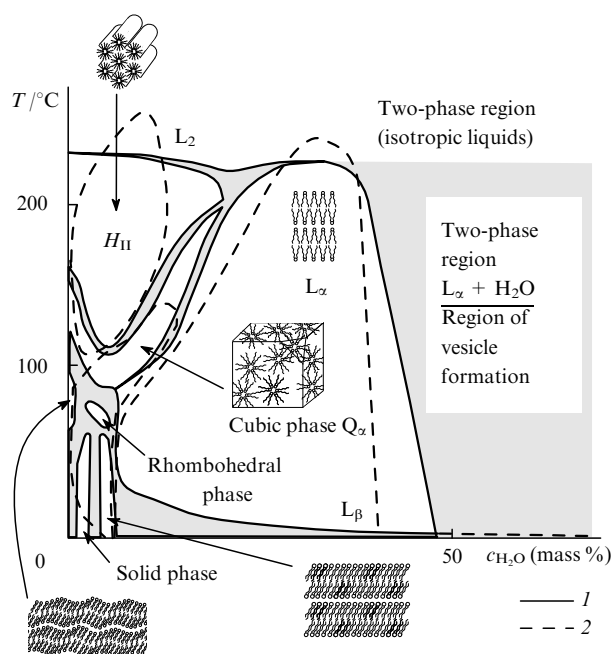


Figure 3. Binary phase diagrams of egg (1) and soybean (2) lecithins.^{10, 13, 58} The basic types of liquid-crystalline structures are shown as schematic insets. For comments, see the text.

H_{II} and Q_{α} occur solely at higher temperatures ($> 90^{\circ}\text{C}$). The phase transition $L_{\alpha} \rightarrow Q_{\alpha} \rightarrow H_{II}$ is induced by the different bilayer expansion in the polar and non-polar regions. Its expansion is larger in the region of hydrocarbon chains due to the thermal activation of *cis-trans*-transitions of C—C bonds.^{25, 27, 28} As a result, the molecule acquires the shape of inverted cone, *i.e.* the magnitude of the dimensionless packing parameter S_p becomes > 1 , and phase transition occurs. The transition $H_{II} \rightarrow L_2$ takes place in sealed tubes at temperatures above 220°C .

When a dry phospholipid is left in air, it absorbs water vapour and adopts the lamellar liquid-crystalline mesophase L_{α} . The quantity of absorbed water is dependent on the air humidity (partial pressure of water vapour). The maximum absorption is 20–21 H_2O molecules per molecule of egg phospholipid.^{37, 38} According to different estimates,^{13, 39–41} the full hydration shell contains from 33 to 39 water molecules, though it is formed only when lecithin is in a direct contact with water.

Hydration is a multistage process. The first solvent molecules are absorbed fairly rapidly. The absorption time constant is below one minute.⁴² The rate of this process considerably decreases as the hydration shell is filled, and in the final stage the absorption time constant is as high as ~ 40 min.⁴²

The water of hydration is believed to consist of three or four types. The first one or two H_2O molecules linked to a lecithin molecule are regarded as the 'inner' or 'strongly bound' water.^{43–45} The use of molecular models⁴⁶ has shown that the energy of their interaction with phosphorylcholine is as high as $30\text{--}40\text{ kJ mol}^{-1}$, while that of the interaction of H_2O molecules with each other in bulk water is only 25 kJ mol^{-1} . Further addition of water induces formation of the basic hydration shell around the polar region of the lecithin molecule. This water type is called 'bound' water because of a markedly lower mobility of H_2O molecules in comparison with liquid water. According to the reported estimates,^{45, 47–50} the quantity of 'bound' water varies from 5 to 11 molecules. The next type is the 'included' or 'trapped' water comprising 4–11 H_2O molecules.^{41, 43, 45, 49, 50} In the final stage, water molecules form mostly an aqueous interlayer between the bimolecular layers. As regards its physicochemical properties, this water virtually does not differ from that in the bulk of aqueous solutions, and this was the reason for calling it 'free' water.

The first 4–5 water molecules are attached to the phosphate group by means of hydrogen bonds and are localised in the region of phosphorylcholine (Fig. 1). The subsequent molecules of the polar solvent penetrate deep enough to reach the hydrocarbon chains and form hydration shells around their carbonyl groups.^{51–53}

The changes in the parameters of the bimolecular layer in the lamellar mesophase L_{α} of egg and soybean lecithins induced by the variation of the water level are shown in Fig. 4. It is seen that under the same conditions, for the lamellar mesophase the period in egg lecithin determined by electron diffraction (curve 1) is somewhat larger than that in soybean lecithin (curve 4). This difference is explained by the higher unsaturation of the latter (Table 1). A detailed picture of osmotic swelling is offered by the example of egg lecithin. The absorption of water leads to the thickening of the layer comprising the bimolecular layer and an aqueous interlayer (curve 1), as well as to the increase in the area A_0 per lecithin molecule in the bilayer (curve 3). At the same time, a decrease is observed in the thickness of the layer formed by the hydrocarbon chains L_{max} (curve 2). The observed thickening of lamellae is achieved through hydration of the polar region of lecithin and the formation of the water interlayer between lamellae.

The area A_0 and the layer thickness L_{max} have been reported⁵⁶ to vary in the opposite ways. This results in a virtual independence of the dimensionless packing parameter S_p of the water content. This finding explains the stability of the bilayer structure and the persistence of the lamellar mesophase (L_{α}) over a wide range of water concentrations.⁵⁶

In conclusion, it should be noted that the presence of 1 mass %–3 mass % of admixtures of ionogenic substances is conducive to a dramatic increase in the extent of lecithin swelling in aqueous solutions (Fig. 4, points 5).^{12, 55, 57, 58} In the presence of ionogenic compounds the thickness of water interlayers may be 4–6 times larger than of lamellae. In this situation, the interval of the lamellar mesophase (L_{α}) occurrence may be considerably extended due to the shift of the right-hand boundary in the binary phase diagram (Fig. 3) towards higher H_2O concentrations (sometimes, up to 85 mass %).⁵⁵ This effect is explained by the electrostatic repulsion of lamellae from each other. This is

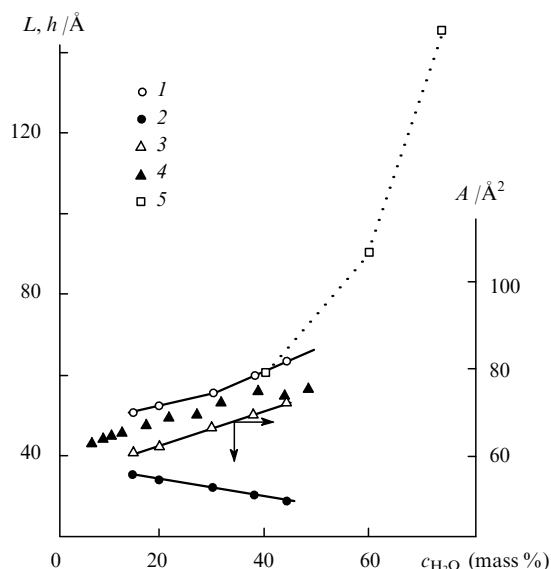


Figure 4. The lamellar mesophase (L) period determined from the results of X-ray diffraction (1, 4, 5), thickness of the hydrocarbon portion of lamellae (h) (2), and the area occupied by a lecithin molecule in the bimolecular layer (A) (3).^{10, 13, 54, 55} Egg lecithin (1–3), soybean lecithin (4, 5), mixture containing 1.5 mass % of cetyltrimethylammonium bromide (5).

confirmed by the absence of the extremal swelling of lecithins in solutions of inorganic salts.⁵⁵

b. Liposomes and vesicles

In the phase diagram region corresponding to the binary system phase L_α –water (Fig. 3), the lecithins placed into water are swelling to form characteristic structures known as ‘myelin figures’ (Fig. 5). They were first described by Virchow⁵⁹ in 1854. The appearance of myelin figures indicates that an amphiphile adopts the form of a lamellar mesophase L_α .⁶⁰

The formation of myelin figures is associated with the expulsion of lamellae from the bulk of a substance as a result of their swelling (for more details, see Refs 61–63). The coaxially arranged bimolecular layers form cylinders which possess high optical anisotropy. The process of swelling is illustrated by a series of photographs shown in Fig. 5. The final stage appears to be highly significant for the problem under discussion. It comprises disintegration of myelin figures into spherical and oval particles (Fig. 5c), whereas the substance bulk is transformed into a sort of paste as a result of swelling. Microscopic examination in the light transmitted through crossed polaroids reveals that the pasty mass formed has a pseudoisotropic texture with oily streaks (Fig. 5d). This type of texture is characteristic of the lamellar mesophase L_α .

Under mechanical impacts (even weak ones), *e.g.*, shaking, the swollen mass is dispersed in the excess of the aqueous solution. Electron microscopy showed⁶⁴ that such dispersions, known nowadays as ‘liposomes’ or ‘vesicles’,[¶] were formed (like an onion bulb) by numerous closed lamellae.

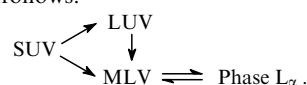
Papahadjopoulos⁶⁵ proposed the following classification of vesicles by size (μm): 0.1–100 — multilamellar vesicles (MLV); 0.02–0.1 — small unilamellar vesicles (SUV); 0.1–1.0 — large unilamellar vesicles (LUV); up to 50 — giant vesicles (GV);

0.02–0.1 — small oligolamellar[†] vesicles (SOV); 0.1–1 — large oligolamellar vesicles (LOV).

The vesicle size is determined by subsequent mechanical impact, its intensity and duration. The diameter of vesicles produced under standard conditions is usually within the limits of 1–4 μm .

Spontaneous formation is observed only in the case of MLV. All other vesicle types can be produced through external impact. The largest energy is required for the production of SUV. This is due to the increase in the free energy during dispersion (Fig. 6).

The increase in the free energy as the vesicle size decreases is caused by an abrupt increase in the interface surface. Consequently, the unilamellar vesicles SUV and LUV turn out to be thermodynamically unstable systems, though they prove to be stable kinetically. With time, the unilamellar vesicles are fused to form multilamellar structures, *i.e.* the system recovers to its initial state. The transitions occurring may be schematically represented as follows:



The result is the separation of a homogeneous dispersion into an aqueous solution and a sediment composed of a mixture of multilamellar liposomes and lamellar mesophase L_α .

Most of the basic techniques for producing vesicles were developed in the 1970s. Their description may be found in a number of surveys (see, *e.g.*, reviews^{66–70}). In the subsequent years, diverse modifications of these techniques were proposed. Information on the basic methods of vesicle preparation, as well as their advantages and drawbacks are listed in Table 2, which also gives values of the inner water volume, accounted for when

¶ The term ‘liposome’ is mostly used in the technical literature. In the scientific literature, dispersions of phospholipids are commonly called ‘vesicles’.

† The term ‘oligolamellar’ means that the vesicular envelope is composed of one to several bimolecular layers. This vesicle type is intermediate between the unilamellar and multilamellar vesicles.

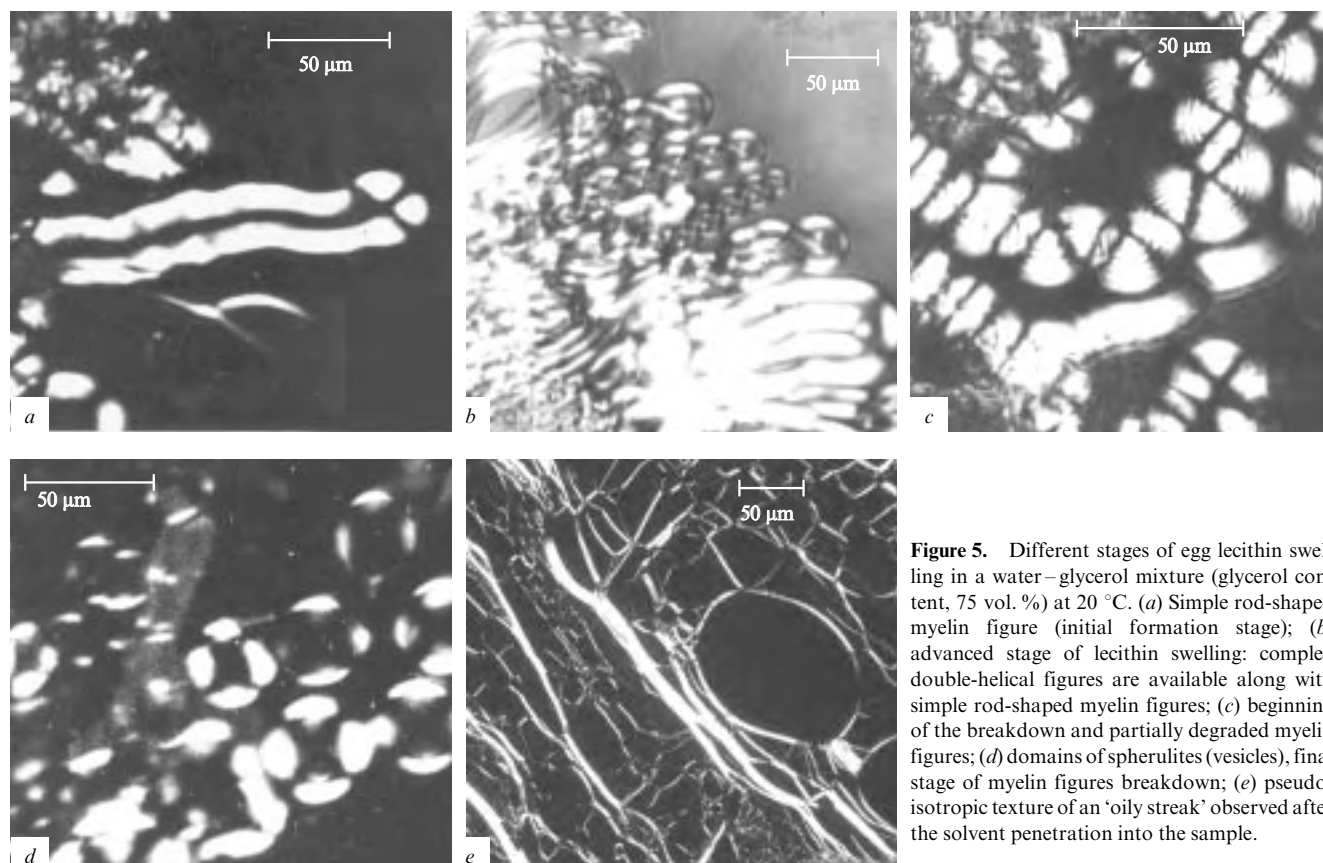


Figure 5. Different stages of egg lecithin swelling in a water–glycerol mixture (glycerol content, 75 vol. %) at 20 °C. (a) Simple rod-shaped myelin figure (initial formation stage); (b) advanced stage of lecithin swelling: complex double-helical figures are available along with simple rod-shaped myelin figures; (c) beginning of the breakdown and partially degraded myelin figures; (d) domains of spherulites (vesicles), final stage of myelin figures breakdown; (e) pseudoisotropic texture of an ‘oily streak’ observed after the solvent penetration into the sample.

Table 2. Characterisation of methods for vesicle preparation.

Method	Basic stages	Type of vesicles prepared	Inner volume, ^a /litre mol ⁻¹	Advantages	Disadvantages	Ref.
Swelling of lecithin in water						
in a flask	1. Dissolution of lecithin in organic solvent. 2. Evaporation of lecithin solution in a rotary evaporator. 3. Addition of water solution to the dry phospholipid. 4. Shaking, stirring, and sonication of lecithin mixture with water solution.	MLV	1–4	The simplest and most accessible method.	1. Heterogeneity of vesicle size. 2. Non-reproducibility of vesicles shell thickness (number of lamellae).	64, 67, 80
on a support	1. Dissolution of lecithin in organic solvent. 2. Transfer of solution onto a special flat support. 3. Drying of solution in vacuum. 4. Addition of water solution to the dry phospholipid.	SUV, LUV, LOV, GV	No data	A simple method for preparing monolayer vesicles.	1. Necessity to add charged surfactants to lecithin. 2. Influence of support on vesicle preparation.	81, 82
Sonication of lecithin-containing solutions	1. Preparation of multilamellar vesicles. 2. Sonication of prepared vesicles.	SUV	0.2–1.5	Uniformity of vesicle size.	1. Intensive sonication. 2. Presence of metal from the dispenser tip. 3. Small volume of inner aqueous solution. 4. Impossibility of incorporating high-molecular-mass compounds into vesicles.	83, 84
Phase reversal	1. Dissolution of lecithin in organic solvent. 2. Addition of water to the dry phospholipid. 3. Emulsification of the mixture by sonication. 4. Concentration of the mixture at 300–400 mm Hg up to the gel formation. 5. Complete removal of organic solvent from the mixture at 700 mm Hg.	LUV, LOV	up to 10	A large volume of inner aqueous solution.	Use of organic solvent.	68, 85
Dispersion of lecithin with detergents	1. Preparation of multilamellar vesicles. 2. Addition of detergent to vesicles. 3. Removal of detergent from the mixture (dialysis, gel-filtration, adsorption, ultrafiltration, centrifugation).	SUV, LUV	up to 4	Suitability for reconstructing lipid-protein complexes.	Use of detergents.	86–88
Injection of solution	1. Dissolution of lecithin in organic solvent. 2. Injection of solution with a syringe into a warm water solution.	SUV, LUV, LOV	~ 0.5 (in the case of SUV)	A fast and simple method for preparing monolayer vesicles.	1. Rapid coagulation of phosphatidylcholine vesicles. 2. Extended range of sizes. 3. Use of organic solvent. 4. Rather high temperatures.	89–92
Double emulsification	1. Dissolution of lecithin in n-hexane. 2. Preparation of water-in-oil emulsion in the presence of surfactant. 3. Partial evaporation of n-hexane. 4. Second emulsification in the aqueous solution with surfactant. 5. Removal of surfactant and n-hexane.	SUV	–	–	Large surfactant content.	93

^a The volume of aqueous solution in the vesicle core surrounded by the phospholipid layer shell characterises the solubilising capacity of vesicles and is expressed in litres of aqueous solution per mole of phospholipid.

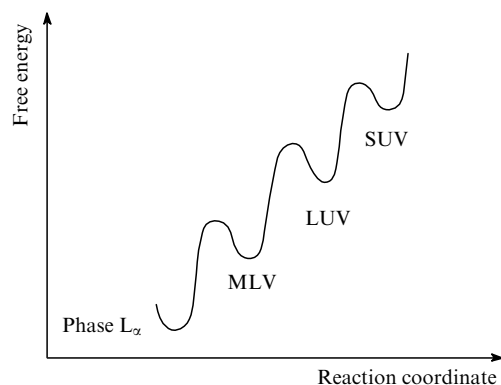


Figure 6. Free energy of a dispersion system for different vesicle types.⁶⁶

incorporating drugs, proteins, DNA, *etc.* into vesicles. The techniques employed for the preparation of unilamellar vesicles are illustrated in Fig. 7.

The mechanism underlying the vesicle formation is not as yet fully understood. Numerous questions remain still unanswered.⁷¹ The most universal model was designed by Lasic.^{66, 72} It relies on the aggregation of the preformed bimolecular 'blocks' into vesicular structures.

Soon after their discovery, vesicles became very popular as models of biological membranes, and they remain active performers of this role until now. Vesicles allow the investigation of the

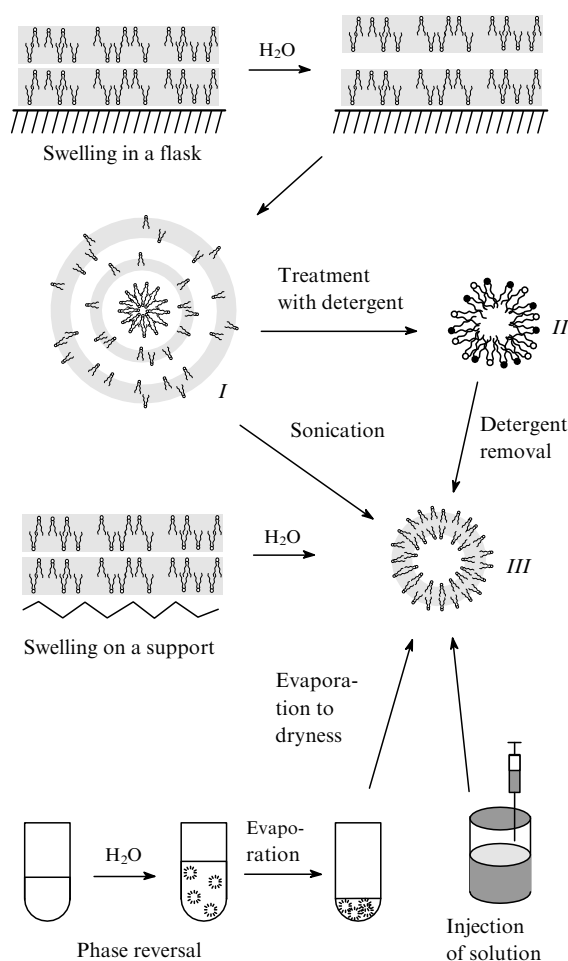


Figure 7. Basic techniques for preparing monolayer vesicles. See Table 2 for details. (I) MLV; (II) mixed micelles; (III) SUV.

transport of various compounds across membranes, membrane fusion, as well as the reconstitution of lipoprotein complexes.^{67, 73–76} The vesicles have acquired wide use in medicine, pharmacology, genetic engineering, cosmetics, and food industries. Today, there are bright prospects for their application in the development of highly specific systems for the targeted transport of drugs and genetic material.^{76–79}

2. Lecithin — organic solvent

Owing to its amphiphilic nature, lecithin is soluble in virtually all organic solvents, except for acetone.^{4, 12, 13} The type of self-organising lecithin structures in solutions is determined by the nature of the solvents. The latter may be divided into two large groups. The first group includes for the most part non-polar solvents in which lecithin forms reverse micelles; the second group comprises polar solvents whose molecules (like water) form numerous hydrogen bonds generating three-dimensional arrays. In these media, the lecithin molecules self-organise to form liquid crystals and display lyotropic mesomorphism.

a. Reverse micelles

The phenomenon of micellisation was studied mostly for egg lecithin.^{94, 95} The critical micelle concentrations have been determined for its solutions in *n*-heptane and benzene. In both cases, the formation of micelles is initiated at a lecithin content of 0.01 μM .^{11, 95, 96} Table 3 lists the aggregation numbers *N* in different solvents, dielectric constants (ϵ) of solvents, as well as conditions of their determination and relevant methods.

Elworthy and McIntosh⁹⁷ have attempted to relate the micelle formation to the dielectric constant of a medium. The magnitude of ϵ was varied by the addition of water or benzene to ethanol. It was found that no aggregates were present in 93% ethanol ($\epsilon = 29.0$). The absence of micellisation was explained by the balance of the solvent interactions with the polar and non-polar lecithin regions. These authors have assumed a medium with $\epsilon = 29.0$ to be the dividing line. The increase in the solvent polarity must initiate the formation of direct micelles, whereas its decrease must stimulate the reverse micelles.

Analysis of the data presented in Table 3 does not reveal any direct correlation between *N* and ϵ . In studies of micellisation, more justified seems to be the approach, according to which the solvent influences the molecular form of lecithin in its aggregates. Certain evidence for this effect may be found in Ref. 95.

In their mixtures with lecithin, non-polar solvents accumulate in the region of hydrocarbon tails that is conducive to a higher effective volume and eventually to the magnitude of the dimensionless packing parameter S_p exceeding unity. For example, the addition of alkanes to the lamellar mesophase L_α (Fig. 3) results in its transition to the inverted hexagonal mesophase H_{II} .^{98, 99} No formation of micelles is observed when the solvent molecules are localised not only near a certain individual group, but occupy the space along the entire lecithin molecule. For instance, under definite conditions such a situation was observed in benzene. Cooling of concentrated solutions led to their thickening. Relevant studies^{100, 101} showed that in this case the reverse micelles are replaced by structures similar in their composition to the lamellar mesophase L_α . In such structures, the benzene molecules are localised in the regions of both the hydrocarbon tails and the polar groups of lecithin and also fill the interlamellar layers. According to the reported results,^{100–103} the localisation of benzene in the polar region is explained by the interaction of benzene with the functional groups of the phospholipid.

b. Non-aqueous liquid crystals

The formation of the lamellar mesophase L_α by lecithin in a water-containing glycerol was first described by Rinne,¹¹⁴ though this report remained mostly unnoticed. The first systematic studies of non-aqueous liquid crystals in ethylene glycol, as well as in alkanediols and low-molecular-mass polyethylene glycols were carried out by Friberg *et al.*^{115–119}

Table 3. Micellisation of egg lecithin in organic solvents.

Solvent	Lecithin concentration /mM	ε^{-1} (Ref. 113)	$T/^{\circ}\text{C}$	N	Method determination of N	Ref.
n-Heptane	≥ 0.01	1.883	25	5	Interfacial tension	11
Benzene	< 0.1	2.284	25	4–6	Osmometry	94, 97, 104
	> 1	2.284	25	> 70	"	97, 104
	13	2.284	40	45	"	105
	10–100	2.284	37	15	"	106
	13	2.284	20	~ 80	Light scattering, viscosimetry, diffusion	46
Toluene	3.7–15	2.379	25; 40	65; 82	Osmometry	107
	3.7–15	2.379			Light scattering	107
<i>o</i> -Dichlorobenzene	15.6	9.93	30	20 ± 5	Ultracentrifugation	108
Chloroform	10–130	4.72	1.5–44	~ 3	NMR	109
Methanol	3–13	32.63	20	3	Light scattering	110
	6.7–27	32.63	25	1	Osmometry	111
Ethanol	3–13	24.55	20	9	Light scattering	110
Butanol	3–13	17.1	20	24	"	110
Hexanol	3–13	13.3	20	28	"	110
Diethyl ether	7–10	4.27	25	~ 40	Ultracentrifugation	112

The interest in mixtures of phospholipids with organic solvents was related, on the one hand, to the problem of perturbation of the intact lipid matrix under the influence of toxic solvents, *e.g.* ethanol. On the other hand, the investigation of lecithin proved to be in the wake of the studies aimed at elucidating the nature of the self-assembly of surfactants in media of different polarity. Nowadays, there are sufficiently settled views on the nature and mechanisms underlying the self-assembly of amphiphiles in organic media.

In organic media, like in water, lecithin can form different types of liquid crystals,^{120, 121} depending on its concentration and temperature. The lamellar mesophase L_{α} is the most characteristic of this phospholipid at room temperature. Excess quantities of glycerol and ethylene glycol cause swelling of lecithin with the formation of myelin figures that further disintegrate into multi-lamellar vesicles.^{60, 63, 122}

The physicochemical properties of solvents, in which the formation of liquid crystals is observed, are listed in Table 4. It also carries characteristics of some solvents, that makes it possible to reveal distinctive features determining the aggregation of amphiphiles.

Analysis of these tabulated data shows that the liquid-crystalline state of lecithin occurs in high-polarity media with a considerable cohesion between the solvent molecules. The latter is characterised by the dipolar angular correlation index and the cohesion parameter.^{113, 123, 124} The ability of solvents to form hydrogen bonds is determined by their donor and acceptor numbers.^{113, 123} The cohesion is seen to be the strongest in the case of water, formamide, glycerol, and ethylene glycol. It is caused by the intermolecular hydrogen bonding. Of note are the maximum values of acceptor numbers of solvents in which liquid-crystalline structures are formed. This may mean that the donor properties are significant for the self-assembly of lecithin.

The above peculiarities of polar organic solvents provided the grounds for suggesting that the necessary condition of the amphiphile self-organisation is the occurrence of hydrogen bondings in the medium.^{120, 121, 125, 126} This suggestion was convincingly confirmed in the experiments with formamide, methylformamide, and dimethylformamide.¹²⁰ Successive methylation of the amino group in these solvents results in the total

Table 4. Viscosity (10^{-1} / Pa s), surface tension (σ / mN m⁻¹), dielectric constant (ε), dipolar angular correlation parameter (g), cohesion parameter ($\sigma / V^{1/3}$ / mN m⁻²), donor number (DN) and acceptor number (E_t) of solvents.

Solvent	η	σ	ε	g^a	$\frac{\sigma}{V^{1/3}}$ (see ^b)	DN^c	E_t^d
Liquid crystals of lecithin are formed							
Water	0.894	72	78.3	2.61	27.7	33.18	63.1
Formamide	3.30	58.2	111.0	2.04	—	24	56.6
Glycerol	945	63	42.5	2.16	15.1	19	57.0
Ethylene glycol	16.9	47.7	37.7	2.13	12.5	20	56.3
Liquid crystals of lecithin are not formed							
Ethanol	1.078	21.9	24.55	3.01	5.7	32	51.9
Acetone	0.304	22.67	20.70	1.21	5.57	17.0	42.2
DMSO	1.996	42.86	46.68	1.08	11.2	29.8	45.1
DMF	0.796	35.2	36.7	1.00	—	26.6	43.8

Note. Abbreviations: DMSO, dimethyl sulfoxide; DMF, dimethyl-formamide. The solvents in which liquid crystals are formed are characterised by the formation of three-dimensional networks of H-bonds; ethanol favours linear chains; in other solvents formation of networks of H-bonds is not characteristic.

^a The dipolar angular correlation parameter indicates the deviation of the electric permittivity from the magnitude that the liquids would have at the same values of polarisability and dipolar moment in the absence of their association. Another meaning: g is the inverse energy of reactive interaction of dipolar molecules; therefore, this parameter is the index of hindrance to their free rotation induced by dipole-dipole interactions. For non-associated solvents, $g \approx 1$. When the liquids are strongly structured and the dipoles are parallel one to another, $g > 2$.^{113, 123} ^b The cohesion parameter proposed by Gordon;¹²⁴ V is the molar volume. For solvents with high cohesion, $\sigma / V^{1/3} > 12.5$ mN m⁻². ^c The donor number of Gutman serves for the quantitative estimation of the basicity of individual solvents.^{113, 123} ^d The acceptor number proposed by Dimrot and Reihardt¹¹³ for the quantitative estimation of the acidity of individual solvents.^{113, 124}

closing of the H-donor centre. It was found that upon transition from formamide to methylformamide, the interval of the lamellar mesophase L_α occurrence is sharply reduced, whereas in dimethylformamide, in which no hydrogen bonds are available, the liquid-crystalline structures are not formed.

It should be noted that the self-organisation of lecithin into the liquid-crystalline state can occur in not all media with intermolecular hydrogen bonds. In this case, an important role is played by the character of hydrogen bonding. A good example are the aliphatic alcohols in which micellisation was found to occur (Table 3), but no liquid crystals were revealed (Table 4). The peculiarity of the aliphatic alcohols is that they form linear hydrogen bonds, which link molecules into chains.^{113, 123} The formation of liquid crystals is observed in solvents (water, formamide, glycerol, and ethylene glycol) with three-dimensional networks consolidated by H-bonds.

Studies of non-aqueous liquid crystals by the NMR and X-ray methods have provided conclusive data on the diminished structural ordering of lecithin molecules upon substitution of organic solvents for water.^{126–128} This is ascribed to the decrease in the solvophobic effect in the series water > formamide, glycerol >> ethylene glycol.¹²⁹ This inference is also confirmed by the fact that micellisation of the same surfactants is initiated in polar solvents at concentrations ~100 times larger than those in aqueous solutions.^{23, 126} As a result, the standard free energy of aggregation calculated by Eqn (5) proves to be smaller by 11–12 kJ mol⁻¹. Interestingly, the increment per methylene group remains unchanged.²³

In the lamellar mesophase L_α , polar solvents form a solvation shell around the polar lecithin region and an interlamellar layer, but they do not penetrate as far as the region of hydrocarbon tails. Investigation of ethylene glycol-containing systems by NMR revealed the existence of three types of its molecules.^{116, 118, 128} The first type is realised when a single diol molecule is attached to the phosphate group of the phospholipid via hydrogen bonds and turns out to be the least mobile. The second type includes up to seven diol molecules. They form the basic solvation shell on the polar portion of the lecithin molecule. Further addition of ethylene glycol induces the third type whose characteristics do not differ from those of the pure solvent. Apparently, the third solvent type comprises free diol molecules localised in the interlamellar layers. The above division of the ethylene glycol molecules into three types in the lamellar mesophase L_α is consistent with what has been proposed for water (see above).

The role of specific solvent in the non-aqueous liquid crystals may be performed by esters of fatty acids and polyethylene glycol. Friberg *et al.*¹³⁰ observed the formation of the lamellar mesophase L_α after mixing lecithin with tetra- or heptaethylene glycol laurate in the absence of any other additives. The period of lamellar structure determined by the method of small-angle electron diffraction diminished with the increase in the content of synthetic surfactant. The same effect took place when the temperature was increased. It has been assumed that the alkyl group of polyethylene glycol laurate is incorporated into lamellae between the phospholipid molecules, while the polyethylene residue acts as a solvent by forming a sort of solvation shell around the polar lecithin region.

The ability of phospholipids to exist in the form of lamellar mesophase L_α in the presence of a variety of organic solvents is of high biological significance.¹³¹ Plant seeds, yeast cells, fungal spores, as well as some microorganisms undergo dehydration during drying. Addition of water causes osmotic swelling and leads to the recovery of their vital functions. A similar cycle is observed in plants preserved in the dehydrated state during the winter season. The removal of water and lower temperatures induce the phase transitions $L_\alpha \rightarrow L_{\beta'} \rightarrow$ crystalline phase (Fig. 3). Hydration causes the reversal to the lamellar mesophase L_α . This reverse transition is the usual cause of perturbations in intact biological membranes.¹³¹ To prevent negative consequences of drying, the living systems have devised a mechanism of stabilisation

of the biomolecular structure of the lipid matrix consisting in the replacement of water by polyols (ethylene glycol, glycerol), disaccharides (trehalose and sucrose), or an amino acid (proline).¹³¹

In this respect, the best studied is the phase behaviour of trehalose-containing systems.^{132–134} The stabilisation seems to consist in the substitution of water and the binding of trehalose hydroxyls to the phosphate group of phospholipids through hydrogen bonds. In this case, the range of the lamellar mesophase L_α occurrence is extended towards smaller solvent concentrations and lower temperatures. The latter circumstance allows polyols, disaccharides, and proline to act as cryoprotectors.¹³¹

V. Ternary systems

In a ternary system containing lecithin, water, and oil, the lecithin molecules are localised at the oil–water interface. Their interaction with two solvents from different phases rather than with one offers additional possibilities for varying the parameters A_0 , $L_{\max}$, V , and S_p .

1. Water-containing systems

a. Swollen micelles

In the case of natural lecithins, the formation of micelles takes place only in organic solvents. Therefore, the further discussion is devoted to the reverse micelles.

Lecithin retains its hygroscopy in the dissolved state, which determines the absorption of water from air by its non-aqueous solutions.^{135, 136} This leads to the dissolution of relatively small quantities of H₂O, from 15 to 30 molecules per phospholipid molecule.^{12, 47, 94, 95, 136–138} The addition of water induces changes in the form of reverse micelles. The spherical shape of aggregates is preserved in aromatic (benzene, toluene) and chlorinated (chloroform, tetrachloromethane) solvents. On the other hand, there is a large group of organic solvents in which the spherical micelles are transformed into cylindrical ones under the influence of traces of aqueous solution (see below).

The first molecules of absorbed water are used to form a hydration shell around the polar head of the lecithin molecule. The hydration pattern has much in common with that described in Section IV.1.a. The differences reside in the number of water molecules: the hydration shell of lecithin in the reverse micelles includes somewhat smaller solvent quantities than, *e.g.*, that in the lamellar mesophase L_α .^{95, 138} The ‘free’ water forms an aqueous core of the aggregates. As the amount of water increases, the radius of the aggregates increases, which provided the ground for calling such micelles ‘swollen’.

The swollen micelles are water droplets surrounded by a monomolecular lecithin layer. Their radius can vary from 10 to 100 Å.⁹⁴ In benzene, for example, the diameter of the water core at the maximum level of the solubilised H₂O is 50±15 Å, whereas in carbon tetrachloride it is 30±5 Å.¹³⁷

The existence of the water core makes it possible to solubilise inorganic and water-soluble organic substances in the non-polar systems with swollen micelles. It is also possible to introduce proteins and to carry out enzymatic reactions in such systems, and this seems to be promising for biotechnological applications.^{94, 139}

b. Organogel

Addition of small quantities of water to non-aqueous lecithin solutions induces their thickening and formation of a gel phase (organogel). The list of organic solvents, in which this phenomenon takes place, includes over 50 names. The presence of organogel in organic solvents was first observed by Scartazzini and Luisi¹⁴⁰ in 1988. An analogous phenomenon was simultaneously and independently observed in a system of immiscible liquids. It was induced by the transfer of water into a non-aqueous solution of lecithin upon application of an electric field.¹⁴¹

The formation of lecithin organogel begins at the level of egg and soybean lecithins of 4–7 g litre⁻¹ (≥ 550 μM).^{140, 142} After the complete dissolution of water, the organogel is outwardly

indistinguishable from the initial solution; it is homogeneous, transparent, and optically isotropic. Differences are revealed upon mechanical impact. The lecithin organogel forms a jelly-like mass. Its viscosity is strongly temperature-dependent. On heating, the organogel is transformed into a non-viscous solution, though it regains its gel-like state on cooling. In other words, jellification is a thermally reversible phenomenon.

An organogel stabilised with lecithin appears to be a thermodynamically stable system. This view is supported by its spontaneous formation. Such a stability is time-limited; the appearance of oxidation products induces degradation of an organogel; their presence also prevents the gel phase formation.¹⁴⁰

The occurring phase and pseudophase transitions, as well as the dependence of static viscosity (η_0) on the number of water molecules (n) per lecithin molecule are shown in Fig. 8 on the example of soybean lecithin solution in n-decane.¹⁴² The initial

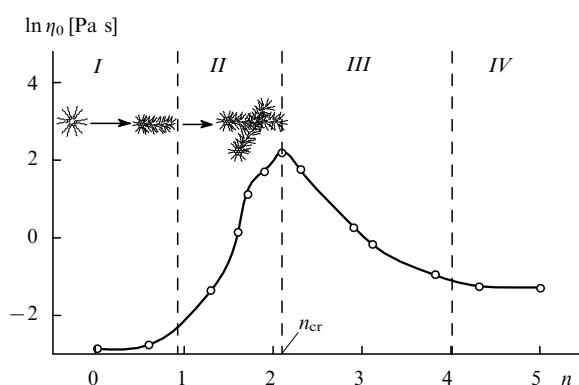


Figure 8. Dependence of the static viscosity of soybean lecithin solution in n-decane (10 mg ml^{-1}) on the number of added water molecules per lecithin molecule (n). The dashed lines indicate the boundaries between different phase and pseudophase states in solution: (I) Newtonian fluid; (II) organogel; (III) non-viscous solution + sedimented organogel; (IV) non-viscous solution + solid sediment. The graph was plotted from the data reported in Ref. 143.

water-free solution containing spherical reverse phospholipid micelles displays properties of a Newtonian fluid.¹⁴³ Upon addition of water, the static viscosity increases proportionally to the quantity of introduced solvent according to the equation

$$\eta_0 = \eta_s(1 + f), \quad (10)$$

where η_s is the viscosity of the initial solution, C is the constant, and f is the solvent volume fraction. The range of linear dependence is not large. Deviation from the linearity is observed when the quantity of added water exceeds $0.5 \text{ H}_2\text{O}$ molecules per lecithin molecule. Within the range from one to two water molecules, η_0 increases more than 10^4 times (Fig. 8). Other rheological parameters (loss modulus G' and storage modulus G'') also abruptly increase.^{143, 144} When the magnitude of η_0 reaches its maximum, the separation of the gel phase into a non-viscous non-aqueous solution and a dense gel begins. In other words, until a certain level, the water acts as a thickener, and then it plays the role of coagulant. It was proposed to characterise this critical concentration by the parameter n_{cr} ^{140, 143} indicating the number of water molecules per lecithin molecule, which corresponds to the maximal water quantity at which the most viscous organogel is formed. The n_{cr} values of non-polar solvents, in which the soybean lecithin forms organogel, are the following: n-hexane, 3; n-octane, 2; n-decane, 2; n-dodecane, 1; 2,3-dimethylbutane, 4; oct-1-ene, 4; octa-1,7-diene, 7; isooctane, 3; cyclohexane, 6; cyclododecane, 12; ethyl laurate, 4; dibutyl ether, 6; tripropylamine, 4; and tributylamine, 2.

The lecithin organogel does not belong to the class of Newtonian fluids. It displays the properties of a viscoelastic (Maxwell-

lian) body.^{143, 144} The rheological behaviour of such bodies is simulated by a spring-piston model, whereas the dependence of dynamic moduli on the frequency of harmonic oscillations is described by the equations¹⁴³

$$G'(\omega) = \frac{G_0 \omega^2 \tau^2}{1 + \omega^2 \tau^2}, \quad (11)$$

$$G''(\omega) = \frac{G_0 \omega \tau}{1 + \omega^2 \tau^2}, \quad (12)$$

where ω is the angular frequency equal to $2\pi\nu$ (ν is the harmonic oscillation frequency), τ is the structural relaxation time, and G_0 is the static modulus. At fast deformations, the lecithin organogel displays properties characteristic of elastic bodies, whereas at slow deformations its properties resemble those of fluids. These states are characterised, respectively, by the static modulus (the high-frequency storage modulus) G_0 and the zero shear viscosity (Newtonian viscosity limit) η_0 (Fig. 8).

Investigations of the lecithin organogel by the methods of light scattering, small-angle neutron scattering, dielectrometry, rheology, electron microscopy, and IR and NMR spectroscopy carried out primarily by Schurtenberger *et al.*^{144–149} and by other researchers^{137, 150, 151} have ascertained changes occurring in the reverse micelles upon addition of water.

Water causes one-dimensional growth rather than swelling of spherical aggregates, which leads to the appearance of giant rod-like micelles (Fig. 8). The size of aggregates increases from 30 to 400–700 Å and may eventually be as high as thousands of angstroms.¹⁴⁹ The transformation of micelles occurs within a narrow range of water concentrations. Addition of 1–3 water molecules per lecithin molecule often proves to be sufficient (Fig. 8). The giant rod-like micelles entangle and form three-dimensional networks.

By its structural organisation and rheological properties, the lecithin organogel resembles semi-dilute solutions of polymers.^{152, 153} A number of other surfactants were found to form gels in aqueous^{152–162} and organic^{158, 163–168} solutions in the absence of polymeric compounds. This provided the ground for segregating micellar gels into a special group. Cates^{169–171} proposed to consider the flexible rod-like micelles as the regular components of the gel phases of amphiphiles. They play the role of polymeric (long-chain) molecules. That is why the giant rod-like micelles are known in the literature as ‘polymer-like’ or ‘worm-like’ micelles. Formation of a three-dimensional network of entangled aggregates in the bulk of solutions determines the visco-elastic properties of the gel-like phases of amphiphiles.

The dynamics of polymer-like micelles was considered by Cates^{169–171} from two different standpoints. On the one hand, aggregates may be regarded as stable flexible rod-like particles, for which a reptation mechanism is applicable. The latter has been proposed for the description of the diffusion of chain molecules in a structured medium.^{172, 173} The migration occurs in an imaginary tubular cavity the dimensions of which are determined by the interactions with the neighbouring molecules. A close analogy may be the movement of individual snakes in their ball. Diffusion in the gels is quantitatively characterised by the relaxation time τ_{rep} required for the particle to migrate at the distance equal to its length.

On the other hand, micelles cannot be regarded as stable formations. They are dynamic structures that are in the process of continuous reversible dissociation and recombination. The amphiphilic molecules pass into solution, reform associations or become involved in exchanges between aggregates;^{14, 23} the aggregates themselves dissociate reversibly into smaller associations. The stability of micelles is characterised by their lifetime τ_b , which is the mean time span between an aggregate formation and its breaking into two parts.

Naturally, the dynamics of polymer-like micelles is determined by the ratio of times τ_{rep} and τ_b . It was proposed to distinguish between the two extreme cases.^{169–171}

1. $\tau_b \gg \tau_{rep}$. The processes of dissociation and recombination are inhibited to such an extent that the micelles may be considered as stable particles whose movement in gel systems follows the reptation mechanism. Such systems may be described within the framework of net theories of polymers.

2. $\tau_b \ll \tau_{rep}$. The dynamics of the processes depends on both the reversible dissociation/recombination of micelles and their diffusion via the reptation mechanism. In this case, the time of structural relaxation is determined by the dependence $\tau \simeq (\tau_b \tau_{rep})^{1/2}$.

The nature of dynamic processes may be clarified by the analysis of concentration dependences of the rheological parameters.^{169–171} The theoretical values of the exponents of lecithin concentrations corresponding to the reptation mechanism and those of polymer-like micelles in the case of G_0 and η_0 are listed in Table 5 along with some experimental values.^{143,144} The variations of G_0 and η_0 are considered as functions of lecithin and water concentrations since the formation and properties of organogels are determined by both components. The best correlation between the experimental and theoretical data is achieved for the dependence of the rheological parameters on lecithin concentration. However, in this case too, a substantial discrepancy is observed. A better fit to experimental data is achieved by employing a more complex model of dissociation/recombination of micelles, though noticeable differences are still found.^{144,170} The participation of water in the self-assembly of lecithin is believed¹⁴³ to be a possible cause of the deviation of parameters from the values calculated on the basis of theory of polymer-like micelles. Usually, the role of solvent in the formation of amphiphilic gels is passive. In a number of cases, the addition of water leads to shortening of cylindrical reverse micelles¹⁷⁴ or to the degradation of organogels.¹⁶⁷ The structure-forming function of H₂O is manifested only in non-aqueous solutions of lecithin. This is the principal difference of lecithin organogels from the gel phases of other amphiphiles. A molecular mechanism of the lecithin self-assembly into polymer-like micelles has been developed and substantiated.^{142,175,176} It is considered below in the discussion of the role of polar solvents.

Table 5. Exponents of concentrational dependences.

Theoretical values		Experimental values	
Reptation mechanism	Polymer-like micelles	Data from Ref. 144	Data from Ref. 143
Concentrational dependence of G_0			
2.25	2.25	2.0±0.1	11
Concentrational dependence of η_0			
3.75	3.5	1.9±0.1	18

In conclusion, it is noteworthy that lecithin organogels have good perspectives for the practical use in cosmetics and pharmacology. Preliminary studies have demonstrated the possibility of incorporation of biologically active compounds, medicinal preparations, and enzymes into lecithin organogels. High viscosity of lecithin organogels makes their use particularly promising as the basic components of creams and ointments for cosmetic purposes, and in the therapy of skin diseases and burns. A number of successful applications of such organogels have been reported.^{177–179}

c. Emulsion

Emulsions are not ranked among thermodynamically stable systems, though they possess the so-called ‘kinetic stability’.^{180–183} In the absence of surfactants, dispersions are extremely unstable and rapidly separate into layers of initial liquids. The coalescence (fusion) of droplets can be prevented, first of all, by a shell formed by amphiphilic molecules adsorbed at the interface of

two immiscible liquids. The scope of this review does not go as far as surveying all the factors determining the stability of emulsions; it is confined to the consideration of peculiarities inherent in lecithin.

Lecithin belongs to the group of effective emulsifiers, *i.e.* emulsions are preserved for an extended time period after dispersion. Since this phospholipid is more soluble in non-aqueous media, one could expect formation of an emulsion of the ‘water-in-oil’ type in accordance with the empirical rule of Bancroft.¹⁸⁴ Nonetheless, in the presence of lecithin, the usual case is dispersion of oil in water.¹⁸⁵ Furthermore, in some instances, spontaneous emulsification takes place.¹⁸⁶

Fairly stable emulsions are formed at an oil–water ratio of 0.4–0.6 and a lecithin concentration above 0.5 mass %.¹⁸⁵ The size of droplets is dependent on the lecithin concentration¹⁸⁷ and varies from 5 to 15 μm .^{185,187}

Lecithin emulsions are characterised by high viscosity levels close to that of gel-like systems. The dramatic growth of viscosity (η) is frequently related to the formation of the lamellar mesophase L_α .^{160,188} This is fully justified in the case of lecithin. Numerous studies^{12,17,58,95,185–187,189–198} have shown that the shell of emulsion droplets is made of a number of bimolecular layers. When present at high concentrations, multilamellar structures can be observed in a polarisation microscope even at a small magnification, owing to anisotropy of the lamellar mesophase L_α . The appearance of the L_α -phase induces a sharp increase in the emulsion stability (see, *e.g.* the papers^{17,95,185–187}). Groves *et al.*¹⁹⁸ believe however that the shell of emulsion droplets does consist of the monomolecular lecithin layer, while the stability is attributed to the formation of multilayer vesicles separating oil droplets.

It should be noted that the multilamellar shell effectively prevents the coalescence of emulsion drops, though it does not prevent flocculation (agglutination).^{185,187} In the course of time, emulsions are observed to separate into a layer of aqueous solution and a concentrated emulsion phase. The multilamellar shell may be regarded as an effective structural-mechanical barrier.¹⁹⁹ Surfactants form usually a monomolecular film around emulsion drops. The more complex structural organisation of lecithin is associated with its proneness to self-assembly into liquid-crystalline structures at the interface of immiscible liquids. The preferential formation of the lamellar mesophase L_α is due to the cylindrical shape of molecules. The insufficient resistance to flocculation is explained by the electroneutrality of the lecithin molecule. This resistance is enhanced by the addition of ionogenic surfactants. Furthermore, the addition of phospholipids carrying other polar groups modifies the dimensionless packing parameter S_p . This enables one to change the emulsion type and enhance its stability, which is widely used for practical purposes.

d. Liquid-crystalline structures

There are numerous studies on ternary systems (see, *e.g.*, Ref. 200); however, no whole phase diagram for the lecithin–water–oil system has been constructed until now. This circumstance does not allow discussion of the general pattern of phase transitions as a function of concentration, although certain features of the phase behaviour of lecithin may be considered.

Most of the studies centred on the transformation of the lamellar mesophase L_α into the inverted hexagonal mesophase H_{II} . The increased interest in this problem was initiated by the hypothesis of the important role of non-bilayer structures in processes occurring in living cells, such as their fusion, endo- and exocytosis, as well as transport of proteins and nucleic acids across biological membranes.^{25,27,201–205} It was presumed that the elucidation of the basic factors determining the phase transition $L_\alpha \rightleftharpoons H_{II}$ would allow a better understanding of the mechanisms for the certain cell processes.

As can be seen in the binary phase diagram (Fig. 3), lecithin occurs mostly in the form of lamellar mesophase L_α . Its transition to the non-bilayer state (the cubic or the inverted hexagonal mesophase H_{II}) takes place on heating. Non-polar solvents induce

this phase transformation at room temperature. For example, the molecules of n-alkanes, the effects of which were most extensively studied by numerous investigators, penetrate between the hydrocarbon chains of phospholipids organised into bimolecular lamellae. This penetration is accompanied by increased lateral pressure in the region of hydrocarbon chains, which results in higher values of the dimensionless packing parameter S_p (Fig. 2) and in the occurrence of the phase transition $L_\alpha \rightarrow H_{II}$.

A thermodynamic approach to the description of phase transition has been developed by Gruner *et al.*^{206–208} According to this approach, the free energy of a system is the sum of three components: the elastic component including all intermolecular interactions, the hydration component, and a component accounting for the packing of the hydrocarbon chains of amphiphilic molecules. Their theoretical estimation proves to be highly problematic because of the complexity of such systems; therefore, phase transitions are considered phenomenologically in terms of the ‘spontaneous’, known also as ‘equilibrium’ or ‘inner’, curvature radius R_0 of the monomolecular layer of amphiphiles. When $R_0 \rightarrow \infty$, the amphiphile molecules aggregate spontaneously into the lamellar mesophase L_α ; when R_0 has a finite value, the monolayer is curved, which leads to the formation of spherical (cubic mesophase) or cylindrical (hexagonal mesophase) aggregates. Specifically, solubilisation of alkanes in the lamellar mesophase L_α induces the decrease of R_0 . In this case, the deformation progresses towards the aqueous solution, which corresponds to the transition to the mesophase H_{II} .^{27, 28, 209}

The lamellar mesophase (L_α) of lecithin solubilises about 8 mass % of n-alkanes.^{99, 210–212} The critical alkane concentration, which induces the phase transition $L_\alpha \rightarrow H_{II}$, is determined by the size of alkane molecule, the degree of phospholipid unsaturation, the lecithin–water ratio, and temperature. The ability of hydrocarbons to induce phase transitions diminishes as the molecular mass increases.^{28, 99, 211, 212} This effect correlates with the decrease in the adsorption and the penetration of n-alkanes into bimolecular layers.^{213–215} In addition, at low water content, non-polar solvents are known to reduce the temperature of the phase transition $L_\alpha \rightarrow H_{II}$ (Fig. 3).²⁰⁹ Unsaturation of lecithin favours phase transformations.^{99, 211, 212} For example, a smaller quantity of hydrocarbon is required for the phase transition $L_\alpha \rightarrow H_{II}$.²⁰⁹

All of the above-discussed effects of non-polar solvents may be explained in the framework of the model of Gruner *et al.*^{206–208} on the one hand, and by the transformation of the cylindrical form of the phospholipid molecule into a conical one, on the other. Clearly, the polar solvents will act in the opposite manner. By forming the solvation shell of functional groups, they increase the effective cross-sectional area of the lecithin polar region. This leads to a decrease in the magnitude of the dimensionless packing parameter S_p , which in turn induces the reversal of phase transitions (Fig. 2). For example, the dissolution of water in a non-aqueous solution of lecithin with inverted spherical micelles (L_2 -phase) initiates the transformation of aggregates into the lamellar mesophase L_α . Lindman *et al.*²¹⁰ observed a more complex phase behaviour. Successive addition of water to the mesophase H_{II} obtained at a definite lecithin–n-alkane ratio induced the following transitions: $H_{II} \rightarrow L_\alpha \rightarrow H_{II}$. The phase transition $L_2 \rightarrow L_\alpha$ usually proceeds with concomitant precipitation.^{4, 13, 15, 17, 94, 135, 136} This effect has found its practical application in the technology of lecithin isolation from soybean oil.⁴

2. Non-aqueous systems

In the discussion of the binary systems, it was shown that the ability of lecithin to self-assemble is preserved upon substitution of water by polar organic solvents. This property of lecithin is observed also in the ternary system lecithin–polar organic solvent–oil, though such systems have been studied to a lesser extent. For example, no reports devoted to liquid crystals are available, although some mention of their existence can be found in the relevant literature. Systematic studies were carried out solely on

lecithin organogels. It should be noted that the formation of microemulsion was observed in non-aqueous ternary systems, whereas in the presence of water only emulsions could be prepared.

a. Organogels: a molecular model of self-assembly

Solubilisation of trace quantities of polar organic solvents in a non-aqueous solution of natural lecithin leads, as in the case of water, to its thickening.^{142, 175, 176} Being a Newtonian fluid, the initial solution is transformed into a viscous-elastic gel-like mass displaying properties of a Maxwellian body. The gel-forming solvents and their critical concentrations n_{cr} , at which the maximal level of viscosity is achieved, are listed in Table 6. Comparison of parameters n_{cr} shows that the gel-inducing efficiency decreases in the series glycerol > water > formamide > ethylene glycol. In some of its properties, the diol occupies an intermediate position between the gel-forming and gel-non-forming additives.¹⁴²

Similarly to water, polar organic solvents induce one-dimensional growth of the reverse spherical micelles. These are trans-

Table 6. Formation of lecithin organogels and physicochemical properties of solvents.^{142, 175}

Solvent	n_{cr}	$10^3 \eta$ /Pa s	σ /mN m ⁻¹	ε	Solubility ^a (%)
Lecithin organogel is formed					
Water	3.6–3.8	0.894	72	78.3	0.01
Formamide	4.6–4.8	3.30	58.2	111.0	0.01
Glycerol	1.7–1.9	945	63	42.5	–
Ethylene glycol	> 5	16.9	47.7	37.7	–
Lecithin organogel is not formed					
1,3-Propanediol	–	39.2	49.2	35.0	0.02
Ethanol	–	1.078	21.9	24.55	0.2
DMF	–	0.796	35.2	36.7	0.08

Note. The organogel-forming solvents and 1,3-propanediol are characterised by the formation of three-dimensional networks of H-bonds; ethanol favours linear chains, while DMF is not characterised by formation of H-bonds. ^a Solubility in squalene; data from Ref. 221.

formed into giant flexible cylindrical aggregates. The molecular mechanism of the lecithin self-assembly into polymer-like micelles has been proposed and substantiated in a number of reports^{142, 175, 176} from IR and NMR spectroscopic studies of the interactions of different polar organic solvents with the phospholipid.

Jellification takes place upon the addition of glycerol, formamide, and ethylene glycol, which form three-dimensional networks through hydrogen bonds. In this case, non-aqueous liquid crystals are also formed. Nonetheless, if the self-assembly of lecithin into liquid-crystalline structures is induced by the solvophobic effects, the roles of polar organic solvents and water in the formation of polymer-like micelles turn out to be different.

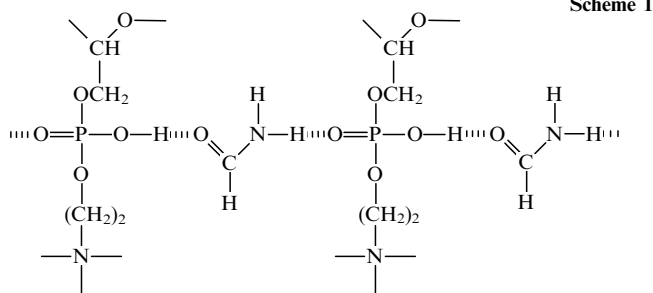
This inference is implied by the fact that the addition of 1–3 solvent molecules per phospholipid molecule (parameter n_{cr}) is sufficient for inducing the gel formation. The totally filled hydration shell of lecithin comprises up to 30 water molecules. In other words, the quantity of polar solvent in polymer-like micelles is insufficient even for the total filling of their solvation shells. Consequently, the polar solvent plays a different role in jellification, which should be regarded as structure-forming.

Comparison of structurally close polar organic solvents may provide a better understanding of the mechanism for the self-organisation of lecithin. The full list of the additives studied to date may be found in Refs 142, 175. We shall confine ourselves to

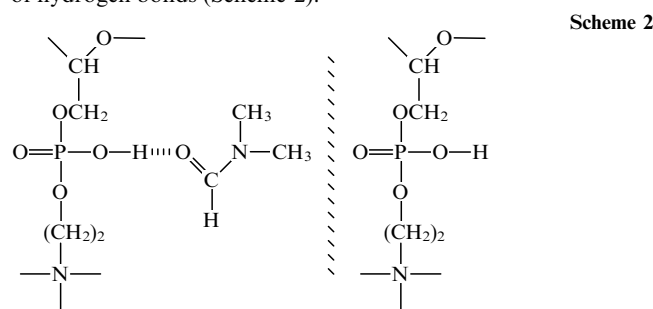
considering the effects of 1,3-propanediol, ethanol, and dimethylformamide (Table 6).

These solvents are structurally close to ethylene glycol, glycerol, and formamide. However, they cannot induce jellification in non-aqueous solutions of lecithin. The IR and NMR studies have shown that the water molecules,^{142, 175, 176, 216, 217} like those of gel-forming organic solvents,^{142, 175, 176} concentrate in the region of the phospholipid polar group by linking to it via hydrogen bonds. 1,3-Propanediol, ethanol, and dimethylformamide also bind with the phosphate residue, though this binding is substantially weaker. The essence of distinctions between the effects produced by the additives that can and cannot induce gel formation may be readily demonstrated by comparing dimethylformamide and formamide.

The molecule of the former carries an acceptor centre (C=O group) and hence can form H-bonds with the donor phosphate group (P—OH). Formamide has larger possibilities since its molecule contains both acceptor (C=O group) and donor (NH₂ group) centres. This allows its linking to the P—OH and P=O groups of phosphate via hydrogen bonding. The polymer-like micelles have been assumed^{142, 175} to form when the molecules of solvents interact simultaneously with the neighbouring lecithin molecules. A possible variant of the structure with formamide is presented in Scheme 1.



The basic distinction between formamide and dimethylformamide, which prevents simultaneous binding of the latter with two lecithin molecules, is that the methyl groups exclude the formation of hydrogen bonds (Scheme 2).



By forming hydrogen bonds with the adjacent phospholipid molecules, formamide acts as a bridging agent. An important aspect is that the phosphate carrying both acceptor and donor groups can also take part in the establishment of several H-bonds.^{113, 123} It has been assumed^{142, 175} that the self-assembly of lecithin into polymer-like micelles is possible because of the formation of extended chains made up of solvent molecules and phospholipid phosphate residues.

Linear networks of hydrogen bonds exert a stabilising effect. This inference was prompted by the comparison of lecithin with didodecyldimethylammonium bromide. This ammonium salt forms, like lecithin, reverse cylindrical micelles, but without participation of H-bonds. The entanglement of micelles produces in the bulk of solutions a similar three-dimensional network, though such micelles do not possess any viscoelastic properties.^{218, 219} Hoffmann¹⁶⁰ has found that the time of structural relaxation (τ) is 10–20 μ s in solutions of didodecyldimethylammonium bromide. After addition of polar solvents to lecithin organogels, *i.e.* after the

appearance of hydrogen bonds, the τ value increases abruptly and amounts to several seconds in the vicinity of n_{cr} .^{142, 143}

The formation of a bridged structure is dependent on the disposition and orientation of solvent molecules relative to the lecithin phosphate group. A possible reason for the lack of jellification after the addition of 1,3-propanediol and ethanol, which can form multiple H-bonds, is thought^{141, 175} to be their insufficiently high polarity (Table 6). It determines both the distribution character of substances in systems of immiscible liquids and their localisation in the interface area.^{161, 180, 220, 221} The lecithin molecule has different polarity regions (Fig. 1). The variation of the dielectric constant [from ϵ (H₂O) to ϵ (oil)] in the monolayer of lecithin occurs not by jumps but rather in a stepwise mode.^{222–224} The molecules of penetrated compounds are localised in different regions along the lecithin molecule according to their polarity.²²⁵ The highest polarity is characteristic of the phosphate group. The probability of a solvent molecule being located near the phosphate group increases with higher solvent polarity. In the series glycerol–ethylene glycol–1,3-propanediol–ethanol, the dielectric constant diminishes, whereas the solubility in the non-aqueous phase increases (Table 6).^{221, 224} The use of the ³¹P NMR method has shown that upon transition from the gel-forming to gel-non-forming additives, the hydrogen bond with the lecithin phosphate group is considerably weakened. This is usually favoured by its curving.²²⁶

b. Non-aqueous microemulsion

Lecithin is known not to form microemulsions in aqueous ternary systems. Microemulsification was found to occur in mixtures with water replaced by ethylene glycol. It is unknown whether or not microemulsions are formed with other polar solvents, since the system soybean lecithin–ethylene glycol–*n*-decane is the only one that has been described to date.^{228, 229} Microemulsions are characterised in greater detail below. Now, we shall consider the picture of non-aqueous microemulsion formation, as reported by Friberg *et al.*^{227, 228}

The area of microemulsion existence in the system lecithin–ethylene glycol–*n*-decane is shown in Fig. 9.²²⁷ At soybean lecithin concentrations of 6 mass %–10 mass %, microemulsification was observed in mixtures where the diol level increased from 30 mass % to 80 mass %. The size of droplets immediately after their preparation was 100–150 nm. Such a water-free microemulsion displayed a limited stability: the separation into immiscible layers began after 10–28 days. Its stability was enhanced with the increasing content of phospholipid and ethylene glycol.

A distinctive feature of microemulsions is their stability during indefinitely long time periods, since they belong to the thermody-

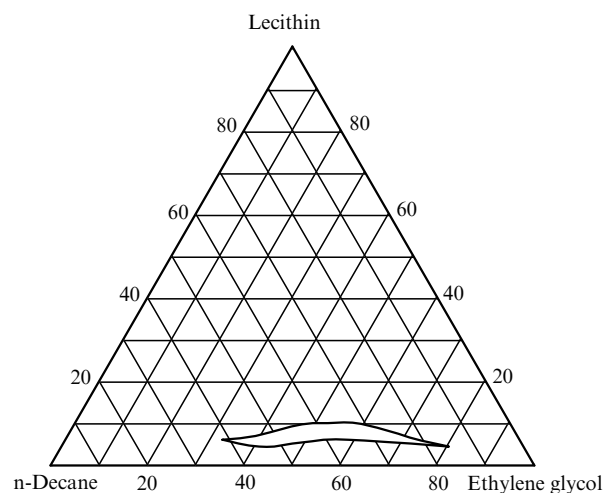


Figure 9. Position of the microemulsion region in the triangular phase diagram of the system *n*-decane–ethylene glycol–lecithin.^{227, 228}

namically stable systems. The separation of a three-component system with time into immiscible layers casts some doubts on the validity of its reference to the microemulsion systems.

Friberg and Podzimek²²⁷ have pointed out the absence of common boundaries between the microemulsional and micellar regions in the phase diagram. This also differentiates the non-aqueous emulsion of lecithin from the known microemulsion systems. The reason for such differences still cannot be identified, since the lecithin microemulsions with ethylene glycol have not as yet been studied to the extent usually required for such purposes. It is hoped that studies of non-aqueous systems along these lines will be reported soon.

VI. Multicomponent mixtures

Mixtures of one or two solvents and different amphiphiles with lecithin are acquiring diverse practical applications. These are already so numerous that merely their listing would require considerable space. The present section is devoted to the basic criteria used for the selection of appropriate components of practically important systems, such as microemulsions and emulsions possessing enhanced stability. In this approach, much attention is given to mixtures of lecithin with other phospholipids and a number of surfactants having important practical and physiological significance.

1. Microemulsions

The term ‘microemulsion’ is used for a dispersion of microdroplets of one liquid in another.²²⁹ This does not, however, necessarily reflect the essence of given dispersive systems and is far from providing their adequate characterisation. The definition proposed by Danielsson and Lindman²³⁰ is gaining popularity over recent years. They refer to microemulsions the water–oil–amphiphile systems that form homogeneous, optically isotropic, and thermodynamically stable liquid solutions. Generally, microemulsions are prepared by adding a third solvent (co-solvent) or a low-molecular surfactant (co-surfactant). It should be noted that the number of ternary systems in which microemulsification can occur is limited. Lecithin belongs to the group of amphiphiles incapable of stabilising the microemulsion phase in the absence of co-solvents or co-surfactants.

The principal difference of emulsion from microemulsion resides in the higher stability of the latter. To understand the reason for different stability, let us express the variation of free energy during dispersion of one liquid in another as

$$\Delta G = \gamma \Delta A - T \Delta S,$$

where γ is the interfacial tension at the oil–water interface, A is the interfacial area between immiscible liquids, and S is the entropy of dispersion. Microemulsification is accompanied by a dramatic increase in the A area. The system is thermodynamically stable when $\Delta G < 0$. In other words, the increase in A must be totally compensated. It has been shown^{231–233} that in some cases this may be done at the expense of the increase in entropy in the course of dispersion. Apparently, the increment ΔA is compensated by the decrease in the interfacial tension. So, in microemulsions containing alkanes, the magnitude of γ diminishes sometimes from $\sim 50 \text{ mN m}^{-1}$ down to $10^{-4} \text{ mN m}^{-1}$,^{23,139} whereas in emulsions it does not drop below 1 mN m^{-1} .

The distribution of microemulsion phases in a three-component phase diagram plotted in the triangular coordinates is presented schematically in Fig. 10 along with the insets showing different dispersive systems. The phase state in the system is determined by the ratio of its components. The single-phase microemulsion is usually localised near the central part of the diagram. The decrease in the amphiphile concentration induces the separation into bi- or tri-phase mixtures. These were first described and classified by Winsor²³⁴, and ever since are referred to by his name.

All the multiphase systems are divided into three types (Fig. 10). Winsor I (WI): microemulsion is in contact with the

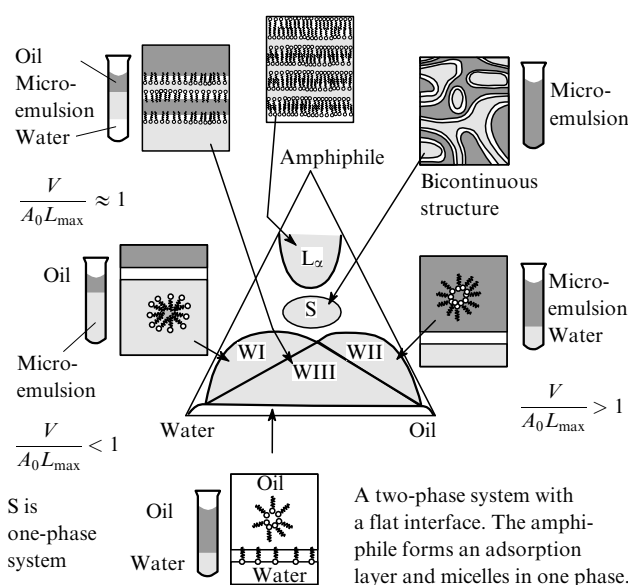


Figure 10. Microemulsion phases in the ternary phase diagram and schematic drawings of dispersive systems. For comments, see the text.

organic phase. Winsor II (WII): microemulsion is in contact with the aqueous solution. Winsor III (WIII) microemulsion separates the organic and water phases. Transitions between states are induced by changes in the system composition or temperature. The most common are the transitions $WI \rightleftharpoons WIII \rightleftharpoons WII$. When the amphiphile quantity proves to be sufficient for the total filling of the interface between immiscible liquids, a one-phase microemulsion is formed instead of WIII. In this case, the ‘phase behaviour’ is often complicated by the appearance of lamellar mesophase L_α .^{23,228,235} In the phase diagram, its region is in contact with the region of one-phase microemulsion (Fig. 10).

A reversible transition from WI to WII is accompanied by the reversal of the sign of curvature $C' = 1/r$ (r is the droplet radius) of the amphiphile monolayer localised at the interface separating two immiscible liquids. For the oil-in-water dispersions, the curvature C' is assumed to be positive, i.e. the monolayer is curved relative to the water. In this case, in the WII system, $C' < 0$. The transition from WI to WII must proceed via an intermediate state with $C' \approx 0$ at $r \rightarrow \infty$. Though the structures formed in this process occur less frequently than the microdrop dispersions, they nonetheless attract the attention of investigators owing to a number of their specific properties. For example, at $C' \approx 0$, one-phase, homogeneous mixtures are produced with the largest content of immiscible liquids, which is highly important for practical purposes. The structures formed at $r \rightarrow \infty$ have come to be known as sponge-like or bicontinuous. They are characterised by the interpenetration of the aqueous and non-aqueous phases with a constant dynamic inversion of ‘water-in-oil’ into ‘oil-in-water’ structures and *vice versa*. This is explained by the proximity of value of the elasticity modulus (K) for an amphiphile monolayer to kT ,²³ which makes the structures sensitive to thermal oscillations. For comparison, the magnitude of K for the condensed monolayers of amphiphiles on the water surface is close to $100 kT$,²³⁶ while in the bimolecular films of egg lecithin it amounts to $10 kT$.²³⁷ Interestingly, the introduction of a bipolar amphiphile (an amphiphile with two functional groups separated by an extended hydrocarbon chain) into lecithin vesicles was observed to reduce the value of K down to $(1.0-0.1)kT$ with the concomitant fast and large-amplitude fluctuations of the bimolecular layer resulting in the appearance of diverse vesicle shapes.^{237,238} A similar pattern of dynamic rearrangements seems to take place in the bicontinuously organised microemulsions.

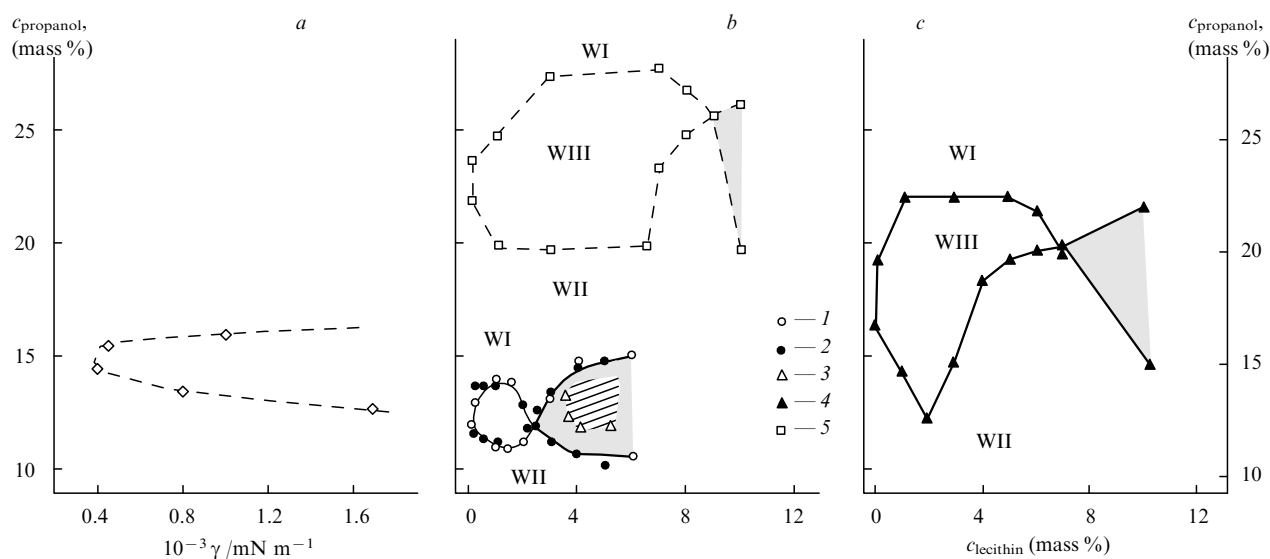


Figure 11. The interfacial tension between aqueous solution and alkane in the system soybean lecithin–water solution of propanol–n-hexane as a function of the propanol content in water (30 °C) (a), and the phase diagrams of the ternary system soybean lecithin–aqueous solution of propanol–n-alkane (25 °C) (b, c). The ordinate, propanol content in water; the abscissa, lecithin concentration in n-alkane. The water : n-alkane ratio = 1 : 1. The region of lamellar L_α phase is hatched; the regions of one-phase microemulsion are marked with grey colour. The system contains n-hexadecane (1–3), n-tetradecane (4), and n-dodecane (5). The diagrams were plotted from the data of Refs 241 (2, 3) and 245 (1, 4, 5).

The role of an amphiphile in the microemulsion systems appears to be crucial. It forms a monomolecular film that separates two immiscible liquids and thereby creates conditions for mixing and simultaneous solubilisation of solvents and compounds with opposite polarities. The resultant balance of molecular interactions turns out to be very sensitive to experimental conditions and the composition of mixtures. Even a slight variation of the latter factors may induce the transitions $\text{WI} \rightleftharpoons \text{WIII} \rightleftharpoons \text{WII}$. On the other hand, phase transitions may also be initiated by changing the form of amphiphile molecules from the inverted to the normal conical shape. In this case, the magnitude of the dimensionless packing parameter must vary successively from 1/3 to 3 (Fig. 2). The shape of molecules cannot change so strongly spontaneously; this may be done only under the action of a number of factors. These include temperature, electrostatic interaction between charged groups, hydration, and the penetration of solvents and co-surfactants into the monomolecular layer of amphiphiles. The magnitude of the dimensionless packing parameter may be regulated by one or all of these factors. They shift the equilibrium in the required direction and induce formation of any of the possible microemulsions or initiate their successive transformations (Fig. 10). Natural lecithin is well-suited for the consideration of the basic regularities of such transitions.

The lecithin molecule preserves its cylindrical form at different water–non-polar solvent ratios, as well as over a wide temperature range.⁵⁶ Besides, lecithin does not reduce the oil–water interfacial tension below 1 mN m^{-1} .^{11, 17, 95} As a result, no formation of microemulsion is observed in the ternary lecithin–water–oil systems. In this case, the only possibility is to prepare emulsions.

First systematic studies of the conditions of microemulsification in the multicomponent systems containing lecithin were carried out by Shinoda *et al.*^{239–243} It was shown that microemulsions are formed upon addition of low-molecular-mass aliphatic alcohols to the ternary system soybean lecithin–water–hexadecane. The addition of co-surfactants induced a sharp decrease in the interfacial tension (Fig. 11). The process of microemulsification was markedly dependent on the alcohol polarity. For example, the addition of butanol led to the formation of reverse swollen micelles. The preparation of Winsor mixtures and one-phase microemulsions was found to require the presence of

ethanol or propanol. The latter was more effective, as microemulsification occurred at its lower concentration. The phase states in the ternary systems with propanol at two levels of soybean lecithin are shown in Fig. 12. It is noteworthy that the area of one-phase microemulsion with bicontinuous organisation is considerably extended with higher phospholipid content.

Thorough investigation of the dependence of microemulsification on the length of lecithin hydrocarbon chains, molecular mass of n-alkanes, and hydrophilicity of aliphatic alcohols has enabled Kahlweit *et al.*²⁴⁴ to reveal a number of regularities making it possible to determine *a priori* the composition of microemulsions intended for different purposes. It was shown that the shorter hydrocarbon chains in lecithin, the more hydrophobic co-surfactants should be used. This is achieved, for example, by substituting butanol for propanol. In the case of didecyllecithin, a further increase in the hydrophobicity of alcohols is required. To this end, the addition of equal amounts of butanol and pentanol was proposed. The increase in the molecular

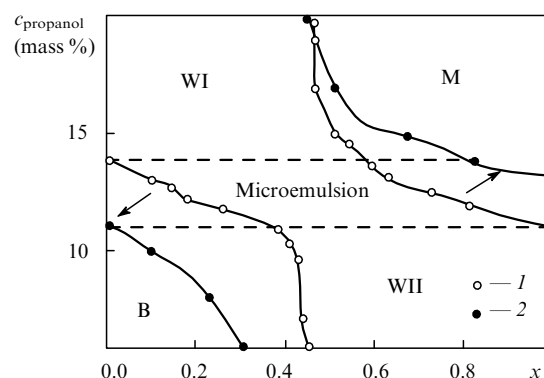


Figure 12. Phase diagram of the system soybean lecithin–water solution–n-hexadecane at 25 °C. The ordinate, propanol content in water. Lecithin concentration in n-alkane: 1 mass % (1) and 3 mass % (2); the arrows indicate the expansion of the microemulsion region with higher lecithin levels. The horizontal dashed lines indicate the boundaries of the single-phase microemulsion. M, non-aqueous phase; B, aqueous phase. The diagram was plotted from the data of Refs 242 and 243.

mass of n-alkanes favours microemulsification in the presence of natural lecithins. This is illustrated by Fig. 11 *b, c*.^{241, 242, 245} On going from n-dodecane to n-hexadecane, the microemulsification is seen to occur at a lower propanol content. Furthermore, a one-phase microemulsion is obtained at a smaller lecithin concentration. The reduction of the molecular mass of n-alkanes and the replacement by aromatic hydrocarbons require a higher hydrophilicity of the aliphatic alcohol. For example, upon transition to n-hexane, propanol proves to be ineffective as co-surfactant because of higher solubility. Preparation of microemulsions requires its replacement by ethanol.

Kahlweit *et al.*²⁴⁴ have proposed to use mixtures of alcohols for the fine regulation of phase equilibria. One should bear in mind that aliphatic alcohols exert toxic effects on living systems. This fact restricts essentially the practical use of microemulsions stabilised by natural lecithins. Non-toxic mixtures containing 1,2-alkanediols as co-surfactants were proposed.²⁴⁶ Besides, n-alkanes were replaced by the non-toxic ethyl oleate. Comparative studies of 1,2-alkanediols have revealed that the optimal conditions for microemulsification in mixtures containing soybean lecithin are created in the case of 1,2-pentanediol whose efficiency is comparable with that of propanol.

In conclusion, it should be said that today the relevant literature carries rather definite concepts of the structure and mechanisms of microemulsion formation. As indicated in a number of recent reviews,^{139, 160, 247–251} the period of intensive studies is giving way to wide and diverse practical applications of microemulsions. The spectrum of their uses proves to be tremendously broad, ranging from chemical and biochemical technologies to functional technologically important fluids, food, cosmetic and medicinal preparations. In this context, it seems appropriate to mention basic advantages that make microemulsions attractive for most varied fields.

1. Universal solvents. As microemulsion systems comprise aqueous and non-aqueous phases, they allow simultaneous solubilisation of both polar and non-polar substances. Consequently, it becomes possible to prepare mixtures of compounds that otherwise cannot exist in direct contact as solutes.

2. Microreactors. In bicontinuous structures, each droplet or domain contains all of the reagents included in a given mixture, which makes it possible to consider them as individual reaction systems. Owing to the size of such microreactors, microemulsions are promising for the synthesis of nanomaterials.

3. Highly effective extraction and reaction systems. High dispersiveness ensures a tremendous interfacial area between immiscible liquids. This intensifies the processes whose rates are limited by migration across the interface or are determined by contacts of substances belonging to different phases.

2. Mixtures with phospholipids and surfactants

In the discussion of emulsions, it was noted that although lecithin is an effective emulsifier, its effect still proves to be insufficiently great. Numerous extensive studies of mixtures of this phospholipid with different substances were, therefore, aimed at enhancing the stability of the emulsions finding most varied practical applications. The present review does not centre on the consideration of numerous experimental data reported to date. Instead, it focuses on the basic principles of the selection of co-emulsifiers illustrated by a number of concrete examples.

The stabilising effect of lecithin is associated with the formation of a multilamellar shell around each emulsion droplet which acts as an effective structural-mechanical barrier preventing coalescence. Despite this, the resistance of droplets to flocculation is not sufficiently high. To eliminate this drawback, methods should be employed that would prevent contacts between the emulsion droplets.

The distance between the bimolecular layers of lamellar mesophase L_α is enlarged by electrostatic repulsive forces (see Fig. 4). Consequently, in order to avert the flocculation of an emulsion stabilised by neutral lecithin, it is necessary to introduce

ionogenic additives. This is achieved through the employment of natural phospholipids, which introduce no toxic properties and do not perturb the biocompatibility with living systems, and by the addition of different ionogenic surfactants.

The set of phospholipids that can acquire an electrical charge via dissociation is rather limited. It includes phosphatidylserine, phosphatidylinositol, and phosphatidic acid. Their addition is conducive to a substantial increase in the resistance of lecithin-stabilised emulsions to flocculation.^{58, 185, 194} These phospholipids have been found to possess different efficiency. This is illustrated by a diagram in Fig. 13. This diagram presents the half-lifetimes of oil droplets from the moment of their contact to fusion measured in model experiments. Accordingly, as regards their efficiency, the anionic phospholipids may be arranged in the following series: phosphatidylinositol < phosphatidylserine < phosphatidic acid. The addition of the latter to lecithin produces the strongest stabilising effect.

Ionogenic surfactants exert analogous effects. A good example are the salts of bile acids, which play an important physio-

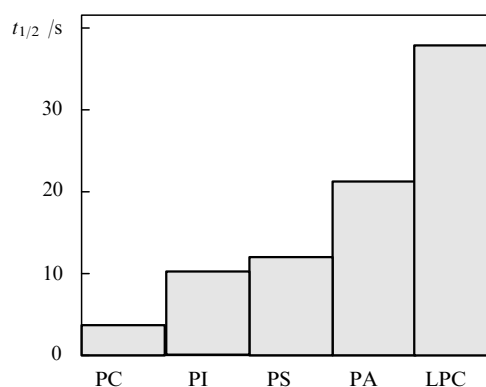


Figure 13. Resistance of oil droplets in water to coalescence.

The non-aqueous phase contains soybean lecithin (PC, 0.1 mM), mixture of lecithin with phosphatidylinositol (PI, 30 mg ml⁻¹), phosphatidylserine (PS, 25 mg ml⁻¹), phosphatidic acid (PA, 15 mg ml⁻¹), and lyso-phosphatidylcholine (LPC, 20 mg ml⁻¹). The ordinate, the half-lifetime of droplets from the moment of their contact to fusion. The graph was plotted according to the data of Ref. 194.

logical role in the processes of fat digestion in the human and animal intestine.²⁵² The major bile ingredients are lecithin and bile acid conjugates, *e.g.*, of cholic acid with taurine and glycine. Their simultaneous presence provides for the emulsification of lipids coming with food. In order to achieve an effective functioning of lipases and subsequent uptake of fatty acids by the intestine walls, the emulsion must be composed of as small droplets as possible and be maintained in the non-flocculated state for a few hours.

The highly significant physiological role of the lecithin mixtures with salts of bile acids stimulated a keen interest shown by different groups of researchers.^{187, 253–256} Studies of the emulsification process *in vitro* revealed that nature had devised a highly effective system. For instance, model experiments¹⁸⁷ showed that the addition of sodium taurocholate to the egg lecithin-stabilised emulsions led to the further increase in their stability. Electrophoretic measurements confirmed that this effect was induced by the appearance of charges on the droplet surface. In addition, sodium taurocholate promoted the formation of a finer dispersion. After its addition, the size of emulsion droplets decreased three to four times.¹⁸⁷ The relevant literature carries indications²⁵⁷ that the presence of sodium cholate can stabilise even microemulsions, although the pertinent processes and the phase behaviour of systems have been little studied.

Another possibility for enhancing the stability of emulsions and modifying their type is offered by the regulation of the dimensionless packing parameter S_p . Lecithin, having an S_p

parameter close to unity, does not possess a molecular geometry optimal for the formation of curved surfaces. This explains wide practical use of additives modifying the dimensionless packing parameter S_p . The surfactants with a large polar region and single hydrocarbon chains diminish S_p , which favours the formation of 'oil-in-water' emulsions, while those with small functional groups and two hydrocarbon radicals induce the formation of 'water-in-oil' emulsions. Let us consider how this is realised in practice.

Lysolecithin, *i.e.* a lecithin derivative in which one of the two fatty acid residues is missing, often serves as an amphiphilic additive with a large polar head. As can be seen from the diagram in Fig. 13, the neutral lysolecithin induces a sharp increase in the stability of lecithin-stabilised emulsions. Its efficiency proves to be substantially higher even than that of ionogenic phospholipids.

As a stabilising additive, lysolecithin has the advantage of being a lecithin derivative. It seems more convenient to perform partial hydrolysis of this phospholipid instead of adding other co-emulsifiers. It has been proposed to use group A phospholipases for this purpose. The enzymatic treatment of lecithin has been shown to result in a substantial increase in the stability of emulsion systems.^{258–260}

The type of emulsion may be changed by the addition of phosphatidylethanolamine. This phospholipid is a lecithin analogue whose molecule includes a quaternary nitrogen carrying three hydrogen atoms instead of three methyl groups. This determines a smaller cross-sectional area of the polar region. As a consequence, the molecule has a conical shape, and $S_p > 1$. Contrary to lecithin, phosphatidylethanolamine forms mostly non-bilayer liquid-crystalline structures, in particular an inverted hexagonal mesophase H_{II} .^{13, 28, 58, 73} Its mixing with lecithin increases the S_p parameter. This leads to the eventual transformation of direct emulsions into their reverse type.^{58, 261}

The efficiency of co-emulsifiers increases when both factors are brought into play, *i.e.* when the droplet surface is charged and the variation of the dimensionless parameter is directional. Sometimes, it is problematic to differentiate them since the molecules of different substances are always different in their shape, while electrostatic interactions affect the magnitude of S_p . The interrelation of these factors may be analysed on the example of lecithin mixtures with sodium taurocholate.

In the study of emulsification, Fillery-Travis *et al.*¹⁸⁷ analysed only the effects associated with electrical charges of droplets. As a matter of fact, the hydrophobic taurocholate anion cannot penetrate inside the bimolecular layer and is most likely localised in the region of the lecithin polar groups. With this distribution, the polar region is expanded, which leads to lower values of the S_p parameter. The decrease in the magnitude of S_p is also favoured by the mutual electrostatic repulsion of molecules in the lateral plane. The mixing of lecithin with taurocholate in the monolayer makes the average molecule acquire the reversed cone shape, which favours the surface curvature and explains the experimentally observed formation of smaller dispersion droplets.¹⁸⁷

It should be noted that the quantitative estimation of the S_p parameter variation in mixtures is a complex, if at all realistic, task. We can predict a general character of changes in the molecular form. The variation of surfactant concentration in mixtures with lecithin induces a series of successive structural rearrangements,^{253–256, 262} which are indicative of a gradual variation of S_p . It seems impossible to establish *a priori* the concentration limits of the existence of different structures. Therefore, appropriate compositions for specific practical purposes are selected on an empirical basis. For example, the German company 'Lucas Meyer', a major producer of soybean lecithin, offers various lecithin-based compositions²⁶³ including lysolecithin, charged phospholipids, and phosphatidylethanolamine as ingredients. Tests of lecithin-based mixtures in technological processes and as components of various systems made it possible to determine their composition ranges for the optimal use in food industry, cosmetics, pharmacology, and paint and varnish production.

VII. Self-organisation of lecithin at the interface of immiscible liquids in the course of adsorption

The investigation of three- and multi-component systems comprising immiscible liquids has shown that their properties and phase behaviour are determined by the state of the amphiphile layer at the water–oil interface. Despite the important role of interfacial films, the problem of lecithin self-assembly in the interfacial regions has not received due attention. Most of the studies were devoted to the monomolecular layer,^{264–271} though even those were not numerous because the priority was always given to the air–water interface.

However, it should be noted that the specifics of experiments with monolayers, such as a limited amount of amphiphile that is added directly at the oil–water interface and the mechanical compression–expansion cycles brought about with the help of a mobile barrier, rule out the occurrence of spontaneous processes. A more suitable approach to the study of the self-organisation phenomena is offered by the method based on the investigation of the course of adsorption, which is not limited by any external factors, after bringing a non-aqueous lecithin solution and water into direct contact, and on the analysis of structures formed in the process of equilibrium onset. Such studies were mostly carried out at the Institute of Chemistry (the Far-Eastern Branch of the Russian Academy of Sciences). The basic results pertinent to the topic of this review are discussed in this section.

Numerous studies were devoted to egg lecithin adsorption from the bulk of n-alkanes at the alkane–water interface.^{11, 17, 95, 272–274} These papers report values of basic thermodynamic and kinetic parameters of egg lecithin adsorption, such as the standard free energy of adsorption (G_{ad}°), diffusion coefficient (D), and the rate constant of lecithin adsorption (β) from the non-aqueous phase at the n-alkane–water interface: $G_{ad}^\circ = -47.6 \text{ kJ mol}^{-1}$, $D = (2.0 \pm 0.5) \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, $\beta = 5 \times 10^{-7} \text{ m s}^{-1}$. The diffusion coefficient is calculated from the equation

$$\Pi = RTC \left(\frac{Dt}{\pi} \right)^{1/2},$$

where Π is the interfacial pressure equal to the difference of interfacial tensions at the oil–water interface in the presence and the absence of lecithin, C is the phospholipid concentration in the non-aqueous solution, t is the time of contact between two immiscible liquids. The diffusional kinetics is characteristic of the initial stages of the adsorption layer formation. As the interface is filled, the diffusional kinetics gives way to adsorptional events. In other words, the entry of the substance into the interfacial film becomes the limiting stage of the process.⁹⁵

The character of the interface filling may be estimated from the dependence of the area per lecithin molecule at the n-alkane–water interface on the concentration of lecithin in the non-aqueous solution (Fig. 14).

Analysis of the peculiarities of the interfacial processes allowed differentiation of at least three concentration ranges in which different types of the adsorption layer are formed.

Dilute solutions (10^{-7} – 10^{-6} M). Lecithin possesses a high surface activity. The change in the interfacial tension begins from the lecithin concentration of about 10^{-7} M. Such a high activity is explained by the large polar region of lecithin (Fig. 1), which does not allow its molecules to remain in the monomeric state in non-polar media, and by the high hydration energy determining the preferential localisation of the phospholipid molecules at the oil–water interface. Thus the standard free energy of lecithin adsorption proves to be of the same order as the hydration energy.^{17, 93}

Relevant studies have shown that within the framework of the classical thermodynamic theory of Gibbs, lecithin adsorption may be described only for strongly dilute solutions. The basic equation used for this purpose is

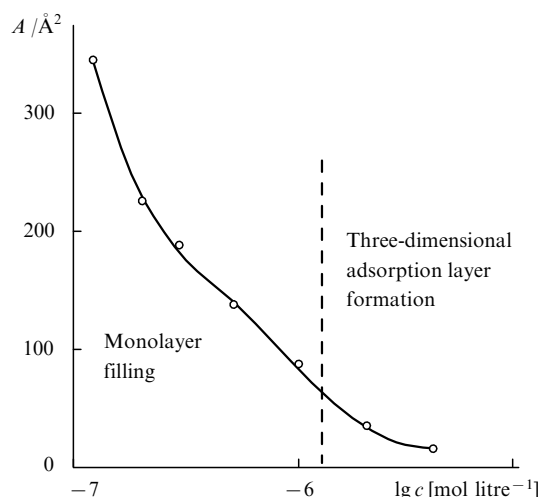


Figure 14. Dependence of the area per egg lecithin molecule at the n-decane – water interface on the concentration in the non-aqueous phase. The dashed line indicates an approximate boundary of the transition from the two-dimensional to three-dimensional filling of the interface. The A values were calculated by the Gibbs equation (3). The interfacial tension was determined using the droplet profile technique which allows measurements after the equilibrium onset in the system (15–17 h).

$$d\Pi = \frac{RT}{AN_A} d\ln C, \quad (13)$$

where N_A is the Avogadro number. The Gibbs equation (13) makes it possible to estimate the area per lecithin molecule in the adsorption layer and to establish thereby the character of the filling of the interface separating immiscible liquids (Fig. 14). At the egg lecithin concentrations ranging from 10^{-7} to 10^{-6} M, the characteristics of its adsorption layer have been found to be close to those of the monolayer.^{17, 95, 272–274}

Intermediate solutions ($> 10^{-6} - 10^{-2}$ M). At the lecithin concentrations above 10^{-6} M, its quantity at the oil – water interface exceeds the level required for the monomolecular filling.^{17, 95, 273, 274} Two-dimensional interfacial films are giving way to the formation of three-dimensional ones. In concentrated solutions, they become distinguishable even at small magnification.^{95, 273} Until now, no special physicochemical techniques have been employed to study the structure of the interfacial layer. This problem is addressed only in rare accounts of experimental observations.

The interfacial structures have been found to display optical anisotropy,^{95, 275} which is indicative of their possible liquid-crystalline organisation. This is consistent with the results from studies of the emulsion droplet shell. More definite ideas of the interfacial layer structure may be derived from experiments on the thinning of non-aqueous films separating two aqueous solutions. It has been shown^{95, 214, 276, 277} that the structure of the adsorption layer resembles the lamellar mesophase L_α . Such a structural organisation is implied by a discrete thinning similar to the successive ‘removal’ of layers with a thickness approximately equal to that of the bimolecular layer.^{214, 277}

It is noteworthy that the formation of three-dimensional structures at the interface of immiscible liquids is not characteristic of surfactants. Generally, the multilayer filling of the interfacial surface takes place, as confirmed by numerous checks of the validity of the Gibbs equation (13). In the case of lecithin, self-assembly of its molecules into more complex structures has been revealed. Hydration of this phospholipid is believed^{95, 273, 274} to be the driving force of this process. Kinetic studies^{95, 273, 274} of the absorption from the bulk of non-aqueous solutions have shown that on reaching the oil-water interface, a lecithin molecule is retained there because of its high hydrophilicity resulting from its hydration with up to 30 water molecules, which considerably

reduces its solubility in the non-polar phase. Lecithin gradually accumulates near the oil – water interface, and when its level becomes higher than that required for monolayer filling, the formation of more complex structures begins.

Concentrated solutions ($\geq 10^{-2}$ M). The interfacial processes spread inside the non-aqueous phase and modify their character. Figure 15 is a photograph illustrating the liquid phase separation near the oil – water interface.^{274, 278} Its appearance in the form of a thin interfacial film is revealed a few minutes after the contact of non-aqueous lecithin solution with water. The film grows thicker, though irregularly. Its surface reveals protrusions directed towards the non-aqueous phase. At a certain moment the film is disrupted allowing a liquid influx to the surface.

Studies of the interfacial processes have led to the conclusion^{274, 278} that it was not a separate liquid phase that was isolated, but rather a dilute non-aqueous solution with a reduced lecithin content. The phospholipid is concentrated in a different, gel-like film in which it is later transformed into a floccular sediment. The gel and the sediment are localised directly on the surface of the water support.

The experimental findings have been used as a basis for developing a mechanism of the interfacial processes^{274, 278} that

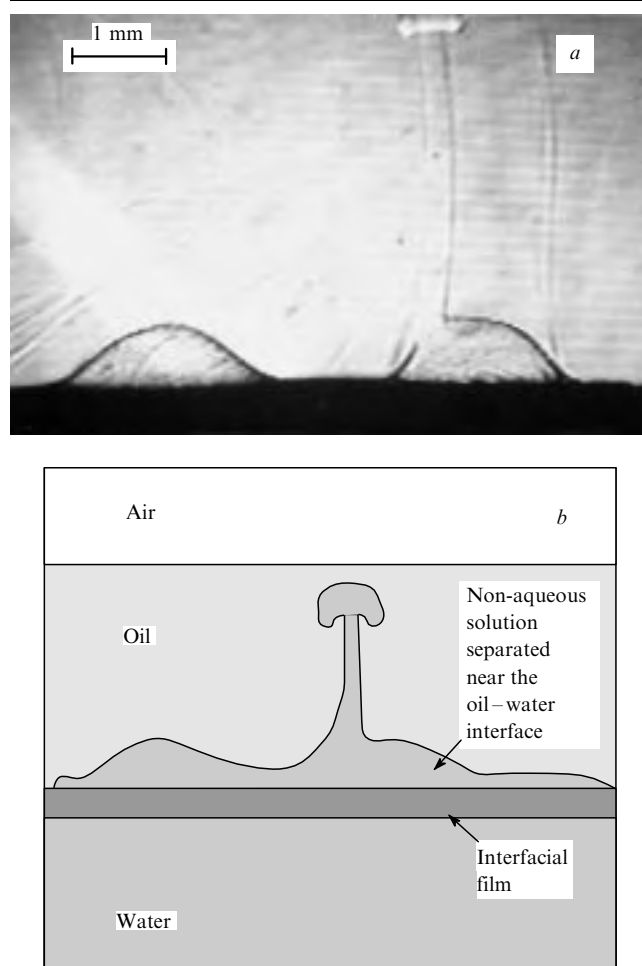


Figure 15. A photograph of the segregated liquid phase in a non-aqueous solution of lecithin near the alkane-water interface at the moment when the liquid is jetting to the alkane surface (a) and a schematic representation of the cell used for experiments (b).

The photograph was taken after a 5.4 min contact of immiscible liquids. Illumination was done with a halogen lamp. For distinct revelation of the segregated liquid phase, the photograph was taken through partially crossed polaroids. Soybean lecithin concentration in n-decane, $10 \text{ mg mlitre}^{-1}$.

relies on the transformation of reverse spherical lecithin micelles into polymer-like aggregates after addition of trace amounts of water. This transformation involves a number of phase and pseudophase transitions: the formation of organogel and its subsequent separation into a compact gel and a dilute non-aqueous solution, and transformation of the gel bulk into a solid sediment (Fig. 8).

In a system of immiscible liquids, the above-mentioned phase and pseudophase transitions are recognised by the appearance of the corresponding phases near the oil–water interface. The respective processes are induced and develop with time owing to the water supply from the adjacent aqueous solution. Since H₂O is insoluble in the non-polar phase, the role of carrier seems to be performed by the lecithin itself. The possible mechanism of such processes may be as follows.

A lecithin molecule attaches water molecules by virtue of hydration at the interface with subsequent desorption of the hydrated molecule and its migration into the bulk of non-aqueous solution, where H₂O is redistributed among non-hydrated lecithin molecules, which induces the transformation of spherical micelles into the polymer-like ones.

It is remarkable that the phase transitions take place not in the adsorption layer but spread considerable distances to occur inside the non-polar phase (Fig. 15). Similar situations are created artificially by bringing into contact two immiscible liquids with one containing a substance that is also well soluble in the second liquid. Its migration may be caused by solubilisation. This may lead to successive phase transitions determined by the phase behaviour of individual amphiphiles.^{180, 279} In the lecithin-containing systems, the migration of water to the non-polar phase is due to different causes, the principal being the hydration of the phospholipid.

The self-organising structures of lecithin modify the interface of immiscible liquids and endow it with new properties. This is especially clearly manifested under external impacts. The application of electric fields has been shown^{17, 95, 274, 280, 281} to lead to the decreased interfacial tension and the emergence of electrodynamic instability at a field strength nearly 100 times as low as that inducing analogous phenomena in the absence of lecithin. Furthermore, the application of a voltage has been found to induce some phenomena that did not occur beforehand: dispersion of a planar interface, the formation of inverted emulsion, and jellification of the non-polar phase. The latter is of interest for practical uses. The substantial decrease in the electric field strength, inducing dispersion of water in oil, allows realisation of processes under mild conditions without high-voltage equipment. Another advantage is that the dispersions formed are preserved only in external electric fields. This makes possible regulation of the processes of the formation and degradation of dispersions.

VIII. Conclusion

The above consideration of the lecithin self-assembly in different media has shown that today it is possible to present a sufficiently full picture of its structures and their phase transformations. One could hardly expect it to be otherwise, since a tremendous number of studies have been devoted to this phospholipid. The investigation of specific aspects of the self-organisation of natural lecithin often gave impetus to the development of new research directions. Liposomes are a good example.

The development of preparative techniques and the use of dispersions as models of cell membranes *in vitro* were for the most part based on lecithin-containing systems. When *in vivo* applications of liposomes were brought onto the agenda, they revealed a number of drawbacks of lecithin among which the principal disadvantage was fast degradation of liposomal structures by cell systems and their insufficient specificity towards the cells selected as targets for biologically active compounds. The efforts aimed at enhancing the stability and targeting the liposomes that involved chemical modification of the lecithin molecule and its complex-

ation with different compounds have resulted in the development of a new generation of liposomal transport systems for biologically active compounds and drugs that has laid the foundation for one of the most rapidly developing directions in biochemistry and biomedicine.^{69, 70, 76–79} Nowadays, further ways for the application of the principles of lecithin self-organisation for devising novel structures are being actively debated in the literature. Specifically, there is a view⁷⁶ that the next stage in the perfection of liposomes will be the development of virus-like systems that would allow a deep insight into the problem of genetic information transfer that is indispensable for the therapy of hereditary diseases or targeted transformations of cell structures for the needs of biotechnology.

The investigation of the self-organising lecithin structures has resulted in the development of a novel type of hemocompatible polymeric material. The basic stages of this work and the application of the principles of lecithin self-assembly have been described in the recent review by Chapman.²⁸² An impetus to the development of this scientific field has been given by the discovery of blood non-coagulation in the lecithin-containing systems. Much work was done to study self-organising structures, such as monomolecular films, liposomes, and liquid crystals that are extensively used as cell membrane models. At the first stage, polymers were produced by polymerisation of the lecithins containing diacetylene bonds in its hydrocarbon chains. It has been found that the incorporation of choline alone proves to be sufficient for making the polymeric materials hemocompatible.

The above-cited examples provide evidence that the potential of the investigation of self-organising lecithin structures has not been exhausted, despite the many-year record of systematic studies. On the contrary, new perspectives seem to appear in this field. They are for the most part related to the study of the lecithin self-assembly in mixtures with biologically active substances, *i.e.* to the investigation of structures that are still closer to the living cell systems.

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Fullerene hydrides: synthesis, properties, and structure

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Abstract. The results of studies on the methods of synthesis of exohedral fullerene hydrides, including the reduction of fullerenes by hydrocarbons, the catalytic hydrogenation of fullerenes, *etc.*, are surveyed. Much attention is devoted to the state of hydrogen in solid fullerene hydrides, the structure of fullerene hydrides, and their reactivity. The bibliography includes 148 references.

I. Introduction

Fullerenes are unique molecules, the reactivity of which has been the object of numerous studies (see, for example, Refs 1–4). Early studies revealed that C_{60} exhibits a high reactivity in relation to nucleophiles,^{1,5–9} free radicals,^{4,10} and the halogens¹¹ and it participates in cycloaddition reactions, including the photocycloaddition of anthracene.¹² These reactions usually result in the formation of a set of products which are difficult to separate and which retain the spherical C_{60} structure. The selective reactions include the osmylation reactions¹³ and the synthesis of fullerene epoxides^{14–16} and fulleroids containing the diphenylmethylene fragment.¹⁷ The reactions involving the addition of metal complexes to C_{60} and C_{70} are controlled by the stoichiometry of the process and the steric loading of the complex.^{18–20} The formation of complexes between fullerenes and low-valence electron-donating metal centres, such as $(Ph_3P)_2Pt(\eta^2-C_{60})$, $[(Et_3P)_2M]_6(\eta^2-C_{60})$ ($M = Pt, Ni$) $(\eta^2-C_{60})IrCl(CO)(PPh_3)_2 \cdot 5C_6H_6$, $(\eta^2-C_{60})RhH \cdot (CO)(PP_3)_2$, $(\eta^2-C_{60})Ru(CO)_4$, *etc.*, in which fullerene acts as a η^2 -ligand, indicates that the double bonds of the fullerene skeleton are electron-deficient. Thus the degree of electron transfer from the metal in the adduct $(\eta^2-C_{60})Ir(CO)Cl(PPh_3)_2$ is similar to that observed in the dioxygen complex $O_2Ir(CO)Cl(PPh_3)_2$.²¹ Calculations of the electronic structure of C_{60} ^{23,24} confirmed that the π -system of the molecule is electron-deficient and that fullerene behaves like a polyolefin rather than an aromatic compound.

The C_{60} structure (I_h symmetry) contains C–C bonds of two types: the shorter double bonds forming common sides of two hexagons (henceforth referred to as the 6–6 bonds)[†] and the longer single bonds, constituting the common side of a hexagon and a pentagon (the 6–5 bonds).^{25,26} In the C_{70} structure (D_{5h}

symmetry), there are five types of carbon atoms and correspondingly eight distinct types of C–C bonds. Four of these constitute the common sides of hexagons, while the other four are formed when five- and six-membered rings fuse.²⁰ Fig. 1 presents the lengths of the 6–6 and 6–5 bonds in the C_{60} molecule, while Fig. 2 presents schematic Schlegel diagrams for C_{60} and C_{70} .²⁷ In the C_{60} and C_{70} fullerenes, the 6–6 bonds are the most reactive and addition to these bonds occurs when fullerenes interact with transition metal complexes (see, for example, Refs 18–22).

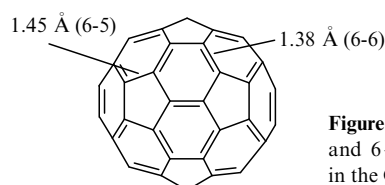


Figure 1. The lengths of the 6–5 and 6–6 bonds and their positions in the C_{60} molecule.

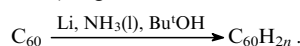
The simplest method for the chemical modification of fullerenes is the hydrogenation of double bonds. The reduction of fullerenes is of great interest because they can serve as an effective medium for the storage of hydrogen.²⁸ Theory predicts that hydrogen atoms may be located both within (endohedrally) and outside (exohedrally) the fullerene spherical surface and that a stable $C_{60}H_{60}$ isomer can be obtained only if ten hydrogen atoms are bound endohedrally in the molecule. Traditional methods of organic chemistry are used in the chemistry of fullerenes for the synthesis of a wide variety of compounds, including hydrogenated derivatives.

The aim of the present review is a survey of the available literature data on the methods of synthesis and studies on the structures and reactivities of exohedral fullerene hydrides. There exist several reviews and monographs in which the problem of the hydrogenation of new carbon clusters is dealt with (see, for example, Taylor and Walton² and Hirsch³), but the rapid development of research in this field requires its special consideration and systematic treatment.

II. Methods of synthesis of fullerene hydrides

1. Birch reduction of fullerenes

The C_{60} fullerene can be reduced by the Birch–Hückel method. According to thin-layer chromatographic data, the reduction produces a single compound (TLC, CH_2Cl_2 :hexane = 1:3, R_f = 0.37).²⁹ On heating, the substance obtained (white or cream coloured) began to darken at 170 °C but did not melt up to 305 °C.



[†] For the numbering of the atoms, see Taylor.²⁷

Table 1. Reduction of the C₆₀ and C₇₀ fullerenes.

System ^a	Substrate : reagent (substrate : reagent : catalyst)	Reaction conditions		Mass spectrometric method ^b	Reaction product ^c	Physicochemical characteristics of fullerene hydrides			Ref.
		<i>T</i> /°C	time /h			<i>P</i> _{H₂} /atm	UV and visible spectra, λ /nm (solvent)	IR, ν /cm ^{−1} (assignment)	
A. Reduction of C ₆₀ fullerene									
C ₆₀ –Li–NH ₃ (l)– Bu ^t OH		−78		EI-MS	C ₆₀ H ₃₆ , C ₆₀ H ₁₈	222 (cyclohexane)	2925, 2855 (C–H), 1620, 1450, 1400, 675	2.5–4.2 with maxima at δ = 3.8 and 3.35 (CDCl ₃)	29
C ₆₀ –Li–NH ₃ (l)– THF–Bu ^t OH		−78		L ² TOF-MS, ICR-MS, SIMS	C ₆₀ H ₁₈ –C ₆₀ H ₃₂				30
C ₆₀ –BH ₃ ·THF	1 : 1	5	0.75	FAB-MS	C ₆₀ H ₂	207.5, 254, 324, 435 (hexane)	1426, 1178, 860 575.5, 574, 566, 552, 550, 545.5, 531.5 and 526.5, 522.5, 517	5.93 (toluene- <i>d</i> ₈)	33
C ₆₀ H ₂ –BH ₃ ·THF	1 : 1	0	0.75	FAB-MS	6 isomers of C ₆₀ H ₄ (1,2,3,4-C ₆₀ H ₄ — 50%) 1,2-C ₆₀ H ₂ (11), 1,4-C ₆₀ H ₂ (5), 1,2,18,36-C ₆₀ H ₄ (1.5), 1,2,3,4-C ₆₀ H ₄ (10.5)	342 sh, 442 (toluene : hexane = 1 : 1)			42
C ₆₀ –N ₂ H ₂	1 : 1000	20	19					6.97 (CS ₂); 5.89 (C ₆ D ₆) 7.23 (CS ₂); 6.13 (C ₆ D ₆) 6.38 (CS ₂); 5.49 (C ₆ D ₆) 5.72 (CS ₂); 4.56 (C ₆ D ₆)	38
C ₆₀ –DHA	1 : 120	350	0.5	FD-MS, FAB-MS, EI-MS	C ₆₀ H ₃₆	230 (CH ₂ Cl ₂)	2913, 2850 (C–H), 1733, 1606, 1511, 1257, 1198, 1169, 1076, 745 2128 (C–D) 2925, 2897, 2854 (C–H)	2.5–4.2 with maxima at 3.3, 3.7, and 4.0 (CDCl ₃)	45
C ₆₀ –DHA- <i>d</i> ₄	1 : 120			FD-MS, FAB-MS, EI-MS	C ₆₀ D ₃₆ C ₆₀ H ₁₈				45
C ₆₀ –DHA	1 : 120	350	24						45
C ₆₀ –DHA–K	(1 : 100 : 5)	250	2	EI-MS	C ₆₀ H _{<i>x</i>} (<i>x</i> = 0–36, 42–44)		2962, 2921, 2853 (C–H) at 4.43, 4.28, 4.20, 4.00, 3.86, 3.45 (CDCl ₃)	3.00–4.70 with maxima at 4.43, 4.28, 4.20, 4.00, 3.86, 3.45 (CDCl ₃)	47
C ₆₀ –DHA- <i>d</i> ₄ – K- <i>d</i> ₂	(1 : 100 : 5)	250	4.5		C ₆₀ D _{<i>x</i>} (<i>x</i> = 0–36)		2153 (C–D)		47
C ₆₀ –H ₂		300–350		ICR-MS	C ₆₀ H _{<i>x</i>} (<i>x</i> = 2–18) ^d				59
C ₆₀ –H ₂ –C ₂ H ₅ I		400	70	FAB-MS	C ₆₀ H ₃₆		2912, 2847, 2827 (C–H), 1655, 1460, 1025, 669		61
C ₆₀ –H ₂ – Pd/C (Pt/C)		180	100	FD-MS	C ₆₀ H ₃₆ , C ₆₀ H ₁₈		2918, 2858 (C–H)	2.5–4.5 (CDCl ₃)	80, 81
C ₆₀ –H ₂ –5% Ru/C		180	2	FD-MS	C ₆₀ H ₃₆ , C ₆₀ H ₃₈ , C ₆₀ H ₄₀ , C ₆₀ H ₄₂	220 (cyclohexane)		2.1–4.25	83
C ₆₀ –H ₂ –5% Ru/C		180	2	FD-MS	C ₆₀ H ₄₂ , C ₆₀ H ₄₆				83

Table 1 (continued).

System ^a	Substrate : reagent (substrate : reagent : catalyst)	Reaction conditions		Mass spectrometric method ^b	Reaction product ^c	Physicochemical characteristics of fullerene hydrides			Ref.
		<i>T</i> /°C	time /h			UV and visible spectra, λ /nm (solvent)	IR, ν /cm ⁻¹ (assignment)	¹ H NMR, δ /ppm (solvent)	
C ₆₀ -H ₂ -5% Ru/C		280	24	120	C ₆₀ H ₄₂ , C ₆₀ H ₄₆				83
C ₆₀ -H ₂ -5% Ru/C		180	2	20-50	C ₆₀ H ₁₈	220, 265 (cyclohexane)		3.0-4.5 (CDCl ₃)	82
C ₆₀ -Zn-acid		110	6		1,2-C ₆₀ H ₂ , C ₆₀ H ₄ , C ₆₀ H ₆				55
C ₆₀ -Zn-conc. HCl		20	1.5		C ₆₀ H ₃₆ (82%),	207, 257, 274.5	2913, 2849 (C-H)	2.5-4.2 with maxima	56
						276.5, 283.5, 292.5,	1725, 1635, 1456,	at 2.55, 2.95, 3.05,	
						300.5, 304.5, 307,	1384, 1273, 1123,	3.3, 3.5, 3.9, 4.0	
						313, 317.5, 320.5, 329	1073, 1035, 730, 678		
C ₆₀ -Zn-conc. DCl					C ₆₀ H ₃₈ (15%), C ₆₀ H ₄₀ (3%)				56
					C ₆₀ D ₃₆ (32%), C ₆₀ D ₃₈ (31%),				
					C ₆₀ D ₄₀ (22%), C ₆₀ D ₄₂ (11%),				
					C ₆₀ D ₄₄ (4%)				
B. Reduction of C ₇₀ fullerene									
C ₇₀ -BH ₃ ·THF	1:2	25			7,8-C ₇₀ H ₂ , 1,9-C ₇₀ H ₂	375, 410 (toluene-hexane)		3.91 s (toluene- <i>d</i> ₈)	43
C ₇₀ -DHA-K	(1:100:5)	250	2.5		C ₇₀ H _x (<i>x</i> = 0-36)	355, 410 (toluene-hexane)			47
C ₇₀ -DHA- <i>d</i> ₄ -K- <i>d</i> ₂	(1:100:5)	250	7		C ₇₀ D _x (<i>x</i> = 0-36)		2923, 2853 (C-H)	2.80-4.60	47
C ₇₀ -N ₂ H ₂	1:1000	20	19		7,8-C ₇₀ H ₂ (1)		2150 (C-D)		38
					1,9-C ₇₀ H ₂ (25)			4.96 (CS ₂); 3.87 (C ₆ D ₆); 5.32, 4.84 (CS ₂); 4.22, 3.71 (C ₆ D ₆)	
					1,3,9,15-C ₇₀ H ₄ (7)			5.312, 4.859 (CS ₂)	
					1,5,6,9-C ₇₀ H ₄ (9)			4.475, 4.127 (CS ₂)	
C ₇₀ -H ₂ -5% Ru/C		100	2	2	C ₇₀ H ₂ -C ₇₀ H ₁₈ , C ₇₀ H ₃₆ (traces)				84
		180	2	20	C ₇₀ H ₃₆	225 (C ₆ H ₁₂)		2.7-4.5 with maxima at 3.35, 3.8 and 4.0	84
C ₇₀ -Zn-conc. HCl		20	1.5		C ₇₀ H ₃₆ , C ₇₀ H ₃₈	207, 223.5, 255, 259, 263, 269.5, 275.5, 278.5	2909, 2852(C-H), 1730, 1456, 1282, 1126, 1035, 750, 730, 695, 587, 468		56
					C ₇₀ H ₄₀ , C ₇₀ H ₄₂ (C ₇₀ H ₄₄)	295.5, 300, 303, 309.5, 312.5			
C ₇₀ -Zn-conc. DCl		20			C ₇₀ D ₃₆ , C ₇₀ D ₄₂ -C ₇₀ D ₄₈				56

^a Designations adopted for the reagents: DHA = dihydroanthracene, K = [7H]benzanthrene catalyst. ^b Designations adopted for the methods: EI-MS = mass spectrometry with sample ionisation by electron impact, L²TOF-MS = laser desorption-laser ionisation time-of-flight mass spectrometry, ICR-MS = ion-cyclotron resonance mass spectrometry, SIMS = secondary ion mass spectrometry, FAB-MS = fast atoms bombardment mass spectrometry, FD-MS = mass spectrometry with field desorption. ^c The ratios of the reaction products are given in brackets. ^d Does not dissolve in the majority of organic solvents.

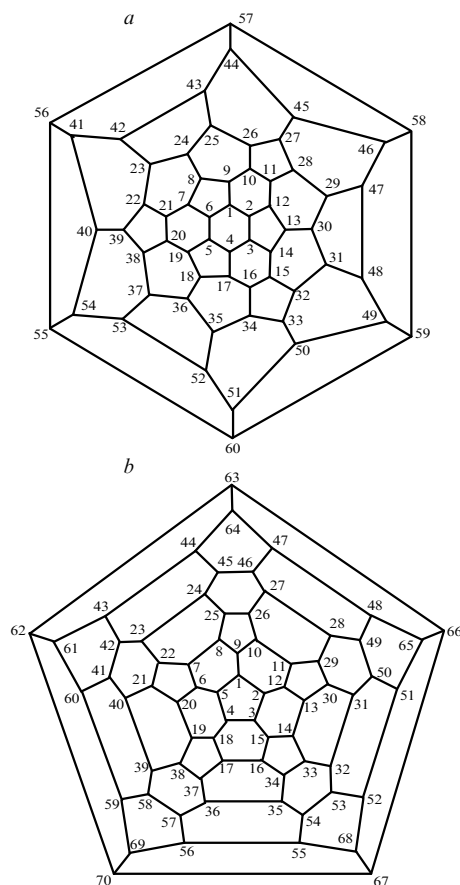


Figure 2. The Schlegel diagram for the C_{60} (a) and C_{70} (b) fullerenes with the numbering of the carbon atoms.²⁷

Mass-spectrometric analysis with ionisation of the sample by electron impact (EI-MS) revealed the presence of two components with m/z 756 (M^+) and 378 (M^{2+}), as well as 738 (M^+) and 369 (M^{2+}), which agrees with the formulae $C_{60}H_{36}$ and $C_{60}H_{18}$ respectively (Table 1). $C_{60}H_{18}$ may be both the product of the direct reduction of C_{60} and the product of the pyrolysis of $C_{60}H_{36}$ formed in the course of the mass-spectrometric analysis. Thorough investigation of the initial reduction product using 'milder' mass-spectrometric methods showed that the Birch reduction leads to the formation of a mixture of polyhydrofullerenes $C_{60}H_{18}$ – $C_{60}H_{36}$, the main product being $C_{60}H_{32}$.³⁰ This experimental distribution of C_{60} hydrides agrees well with the distribution of the products calculated by approximate methods on the assumption that the Birch reduction does indeed involve 1,4-hydrogen addition to the cyclohexadiene fragments of C_{60} (Table 2).³⁰

Treatment of a toluene solution of the fullerene reduction product with a strong oxidant — 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) — leads to C_{60} on refluxing. Thus the reduction of C_{60} is fully reversible and the C_{60} skeleton does not break down in the course of the reaction.²⁹

Under the conditions of the Birch reduction, the C_{70} fullerene affords $C_{70}H_{30}$ as the main product. It has been suggested that the most stable fullerene hydride is obtained as a result of the 1,4-addition of hydrogen to the double bonds on the C_{70} surface.³¹

Benzene may serve as the source of hydrogen in the reduction of fullerene by metallic potassium in the presence of crown-ethers (18-C-6).³²

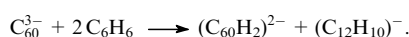
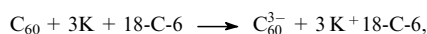


Table 2. Experimental and calculated (numerical modelling of 1,4-addition by the Monte Carlo method) distributions of the products of the Birch reduction of C_{60} .³⁰

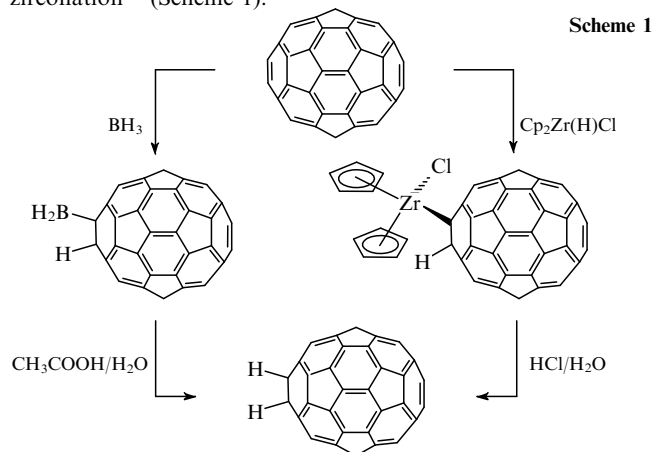
Composition	Distribution of polyhydrofullerenes produced (% of main peak)	
	experiment ^a	calculation ^b
$C_{60}H_{24}$	39(24)	0.2
$C_{60}H_{26}$	53(35)	3
$C_{60}H_{28}$	72(57)	19
$C_{60}H_{30}$	96(89)	53
$C_{60}H_{32}$	100(100)	100
$C_{60}H_{34}$	71(62)	98
$C_{60}H_{36}$	11(10)	55
$C_{60}H_{38}$		14
$C_{60}H_{40}$		0.3

^aThe results of SIMS are quoted. The results of ICR-MS with laser desorption are given in brackets. ^bThe calculation is based on the reduction of 20 000 C_{60} molecules.

2. Reduction of fullerenes by hydrides

The number of thermodynamically and kinetically stable isomers of the simplest fullerene hydrides ($C_{60}H_2$ and $C_{70}H_2$) is small.

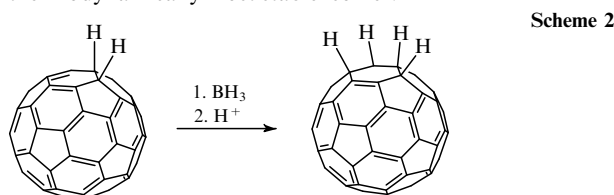
Thus the reduction of C_{60} to $C_{60}H_2$ can lead to the formation of 23 isomeric dihydrides, two of which are the products of the 1,2- or 1,4-addition to the 6–6 bonds and have the lowest heats of formation, the latter isomer being less stable to the extent of 3.8 kcal mol^{−1}.³³ A two-stage process (the hydrometallation of C_{60} and C_{70} with subsequent hydrolysis), occurring with high regioselectivity, is a convenient method of synthesis of the lowest fullerene hydrides, which has been demonstrated in relation to the synthesis of $C_{60}H_2$ and $C_{70}H_2$ by hydroboration³³ or hydrozirconation³⁴ (Scheme 1).



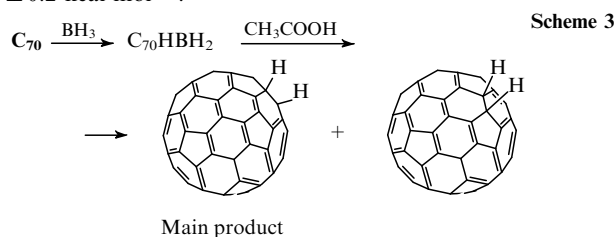
The interaction of C_{60} with $BH_3 \cdot THF$ in toluene at 5 °C (Table 1) with subsequent hydrolysis leads to a 10%–30% yield of $C_{60}H_2$ — the simplest fullerene hydride,³³ which was isolated with the aid of high performance liquid chromatography (HPLC). The formation of the stable $C_{60}H_2$ isomer is consistent with calculations.^{35,37} The ^1H NMR spectra of $C_{60}H_2$ as well as $C_{60}HD$, prepared by the reaction of the intermediate $C_{60}HBH_2$ (Scheme 1) with CH_3COOD or D_2O , agree with the spectra of the products of the hydroalkylation of fullerene.³⁶ The regioisomer obtained is the product of 1,2-addition to the 6–6 bond. As in the case of 1-organo-1,2-dihydrofullerene,³⁶ the protons of the dihydrofullerene $C_{60}H_2$ give rise to a signal in the ^1H NMR spectrum at $\delta = 5.9$ ppm (toluene- d_8).³³ The second stable isomer ($\delta = 6.13$ ppm) was detected in this system in a significantly smaller amount.³⁸ The presence of a band at 430 nm in the electronic absorption spectrum of the brown solution of $C_{60}H_2$ is a characteristic property of C_{60} 1,2-adducts.³⁹ The interaction of C_{60} with an excess of $BH_3 \cdot THF$ and subsequent hydrolysis of the

resulting complex with either glacial CH_3COOH , $\text{NaOH} - \text{H}_2\text{O}_2$, or NaOH leads in the presence of atmospheric oxygen to the water-soluble fullerols $\text{C}_{60}(\text{OH})_x$. When the IR spectra of the reaction products obtained under an inert atmosphere and in the presence of atmospheric oxygen were compared, it was found that the reaction proceeds via the oxidation of the C–H bonds in the hydrofullerene formed initially.⁴⁰ A similar process has been observed also in the reduction of C_{60} by tetrabutylammonium tetrahydroborate in benzene at room temperature.⁴¹

The hydroboration of the dihydride C_{60}H_2 (Scheme 2) leads to the formation of a mixture of six isomeric compounds C_{60}H_4 in ~10% yield, among which 1,2,3,4- C_{60}H_4 with all four hydrogen atoms added to neighbouring 6–6 bonds, is, according to ^1H NMR data, the main (~50%) reaction product.⁴² It is also the thermodynamically most stable isomer.



The interaction of C_{70} with $\text{BH}_3 \cdot \text{THF}$ (Table 1, Scheme 3) takes place, in contrast to C_{60} , at room temperature and leads to a ~20% yield of a mixture of 1,9- and 7,8- C_{70}H_2 in the ratio of 2 : 1, for which the difference between the free energies is $\Delta G_{295} = 1.4 \pm 0.2 \text{ kcal mol}^{-1}$.⁴³



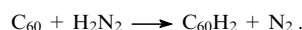
According to calculations,³⁷ the products of the 1,2-addition of H_2 to the 6–6 bond of the C_{60} and C_{70} fullerenes and the products of addition in the *para*-position in the six-membered ring have the lowest energy. Both C_{70}H_2 isomers isolated are the products of 1,2-addition. The 7,8- and 1,9- C_{70}H_2 isomers are not interconverted either on standing at room temperature for several weeks or on heating up to 100 °C for 1 h. However, in the presence of Pt/SiO_2 at room temperature, 7,8- C_{70}H_2 in solution in toluene is converted into a mixture consisting of the 7,8- C_{70}H_2 , 1,9- C_{70}H_2 formed as a result of isomerisation, and C_{70} obtained on decomposition.⁴³ The 7,8- C_{70}H_2 isomer is less stable than the 1,9-isomer, but both are stable for a long time at –20 °C in toluene or hexane. Both substances are more sensitive to the action of light and air than C_{60}H_2 .

The structures of the C_{70}H_2 isomers obtained have been confirmed by ^1H NMR spectra: the 7,8- C_{70}H_2 protons give rise to a singlet with $\delta = 3.91 \text{ ppm}$, while the 1,9- C_{70}H_2 protons generate a quartet with the centre at 4.0 ppm. The electronic spectra of the C_{70}H_2 isomers differ appreciably from the absorption spectrum of C_{70} and may be useful for the identification of the C_{70} adducts.⁴³

The interaction of organometallic compounds with fullerenes proceeds exclusively at the 6–6 bond.^{18–22} Thus hydrozirconation opens a path to the selective synthesis of functional derivatives of fullerene. The product of the hydrozirconation of C_{60} is a zirconium(IV) complex, namely $[(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}]_n\text{C}_{60}\text{H}_n$, where $n = 1, 2$, or 3. Hydrolysis of this intermediate leads to a mixture of fullerene hydrides, among which the main product is C_{60}H_2 (Scheme 1).³⁴ The dihydride C_{60}H_2 obtained in this way has been characterised with the aid of ^1H NMR, IR and UV spectroscopy, and mass spectrometry.[‡]

‡ C_{60}H_2 : M^+ , m/z 722; IR (KBr), $\nu/\text{cm}^{-1} = 2956, 1427, 1327, 1259, 1184, 1042, 791, 728, 725, 599, 590, 574, 565, 550, 527, 478$; UV and visible spectra, $\lambda/\text{nm} = 486, 457, 431, 404, 322, 308, 256$, and 212.

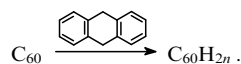
Other methods for the reduction of C_{60} and C_{70} fullerenes have also been described, for example reduction by hydrogen in the presence of 5% Pt/C , by $\text{Cr}(\text{II})$ acetate, and by diimide.³⁸ A change in the spectroscopic characteristics of the reaction mixtures in the visible region was noted in all cases. Peaks with $\delta = 5.9$ and 6.1 ppm were observed in the ^1H NMR spectra of C_{60} fullerenes. They refer to reduced C_{60} derivatives.^{33, 38} The fullerene derivatives obtained on treatment with $\text{Cr}(\text{II})$ acetate or with hydrogen in the presence of 5% Pt/C are unstable in the light; in the presence of atmospheric oxygen, they are converted into fullerols. On the other hand, the products of the reduction of C_{60} and C_{70} by diimide are formed in a high yield; the reaction is distinguished by its simplicity. This method is convenient for the synthesis of the di- and tetra-hydride derivatives of fullerenes.



The main product of the reduction of C_{60} by diimide is the 1,2,3,4-tetrahydrofullerene C_{60}H_4 ; apart from this compound, other C_{60}H_4 isomers and more highly hydrogenated compounds are also formed. When C_{70} was reduced with diimide, eight products were obtained: two of these were characterised as the tetrahydrides 1,5,6,9- C_{70}H_4 and 1,7,8,9- C_{70}H_4 and a further two were characterised as the dihydrides 1,9- C_{70}H_2 and 7,8- C_{70}H_2 identical to the compounds obtained previously by reduction with diborane.⁴³ It has been noted that the hydrogenated fullerene derivatives dissolve more effectively in CS_2 than in benzene or toluene. The chemical shifts of the ^1H NMR signals strongly depend on the solvent: in CS_2 , they undergo a downfield shift (by 1 ppm) compared with benzene.

3. Reduction of fullerenes by hydrocarbons

At elevated temperatures, fullerenes serve as dehydrogenating agents in relation to hydrocarbons. Thus treatment of C_{60} in a sealed glass tube at 350 °C under an inert atmosphere with a melt of 9,10-dihydroanthracene (C_{60} :9,10-DHA = 1 : 120), which serves as a source of hydrogen, leads to rapid (30 min) decolorisation of the melt.



It has been found that the reduction of the C_{60} fullerene under the conditions of the noncatalytic transfer of hydrogen atoms from the donor to the acceptor (transfer hydrogenation)⁴⁴ leads to the hydrides $\text{C}_{60}\text{H}_{36}$ and $\text{C}_{60}\text{H}_{18}$.⁴⁵ In this reaction, fullerene can function as a radical trap.⁴⁶

After the sublimation of the excess DHA and of the anthracene produced, a white (or slightly yellowish) solid product $\text{C}_{60}\text{H}_{36}$ was isolated and was characterised by mass spectrometry. A peak at m/z 756 corresponds to it. The increase in reaction time to 24 h leads to the formation of a coloured product with m/z 738, which corresponds to the compound $\text{C}_{60}\text{H}_{18}$. The presence of a hydride having this composition has also been confirmed by thin-layer chromatography.⁸ At the same time the free C_{60} fullerene was detected in the melt. EPR study of this reaction showed that the 9-hydroanthryl radical is formed as an intermediate. $\text{C}_{60}\text{D}_{36}$ and $\text{C}_{60}\text{D}_{18}$ are formed similarly when dihydroanthracene-*d*₄, deuterated in the 9- and 10-positions, is used for the reduction of fullerene. Cyclohexa-1,4-diene has been used in the hydrogenation of C_{60} by the method of transfer hydrogenation.⁴⁵

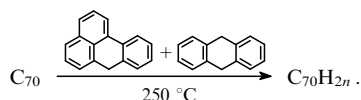
Solutions of $\text{C}_{60}\text{H}_{36}$ in a series of organic solvents are unstable even under an inert gas atmosphere. After a time, they become turbid and the signals in the ^1H NMR spectrum become broadened. Heating of the hydrides $\text{C}_{60}\text{H}_{36}$ and $\text{C}_{60}\text{H}_{18}$ in an inert gas (550 °C, 15 min) leads to their quantitative dehydrogenation to C_{60} . Anthracene and α -methylstyrene may serve as chemical dehydrogenating agents for the hydride $\text{C}_{60}\text{H}_{36}$ (the reduction of

§ SiO_2 , CH_2Cl_2 :hexane = 1 : 3; $R_f(\text{C}_{60}\text{H}_{36}) = 0.37$ ^{29, 45} and $R_f(\text{C}_{60}\text{H}_{18}) = 0.15$.⁴⁵

anthracene affords 1,2,3,4-tetrahydroanthracene, which is inert under these conditions).⁴⁵

The conclusion about the structure of $C_{60}H_{36}$ obtained by the method described by Rüchardt *et al.*⁴⁵ was reached on the basis of the inability of the latter to be reduced to the corresponding radical-anion[¶] on treatment with metallic potassium in dimethoxyethane. According to the authors,⁴⁵ this indicates the presence of isolated C=C bonds in the $C_{60}H_{36}$ molecule, as has been postulated for the product of the Birch reduction.

[7H]Benzanthrene plays the role of a catalyst in the hydrogenation of C_{60} and C_{70} by the method of Rüchardt *et al.*⁴⁵ using dihydroanthracene as the reducing agent (fullerene:catalyst:DHA = 1:5:100).⁴⁷



The use of a catalyst made it possible to reduce the reaction temperature from 350 °C (for the noncatalytic reaction) to 250 °C, but the selectivity of the reaction became lower under these conditions. The C_{70} fullerene reacted more slowly than C_{60} . Deuterio-derivatives of C_{60} and C_{70} have also been obtained by this method. The mass spectra of the reaction products formed in the presence of the catalyst are characterised by a wide mass distribution (Table 1). According to a mass-spectrometric study with ionisation of the sample by electron impact, in the case of C_{60} a hydride with a higher hydrogen content, namely $C_{60}H_{44}$, may be obtained under the conditions of the catalytic reaction. On the other hand, the mass spectra of the products of the reaction with ionisation of the sample by laser desorption (LD-MS) were identical with the spectra of the products obtained in the noncatalytic reaction, which indicates the same degree of reduction of C_{60} and C_{70} in both cases, namely to $C_{60}H_{36}$ and $C_{70}H_{36}$. This feature of the LD-MS method has also been noted by other researchers and has been explained by the possibility of the elimination of hydrogen from the unstable hydrides on laser desorption.

It is of interest that the main peak in the EI-MS of $C_{70}H_{36}$ (at m/z 876) indicates an increased stability of the hydride with 36 hydrogen atoms. The enthalpy of formation of $C_{70}H_{36}$ has been calculated: $\Delta H_f^\circ(\text{gas}) = 490.2 \text{ kcal mol}^{-1}$.⁴⁷ Further reduction of C_{70} to $C_{70}H_{40}$ leads to an increase in $\Delta H_f^\circ(\text{gas})$ to 535.7 kcal mol⁻¹. Consequently the formation of $C_{70}H_{36}$ is the thermodynamically preferred process.

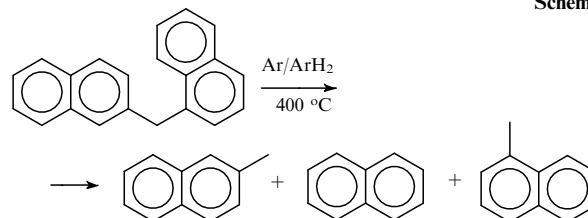
When C_{60} and mesitylene were refluxed (163 °C) under an inert atmosphere for 24 h, both the products of the dimerisation of mesitylene and the product of its addition to C_{60} were detected in the reaction mixture (C_{60} adducts with one, two, and three mesitylene residues), the yield of the products of the oligomerisation of mesitylene (dimers and trimers) exceeding by a factor of 7 the initial C_{60} concentration. One may therefore speak in this case of the catalytic activity of the C_{60} fullerene.⁴⁸

The influence of C_{60} on the dehydrogenation of hydroaromatic compounds on heating has also been mentioned by Malhotra *et al.*⁴⁸ For example, in the dehydrogenation of 9,10-dihydrophenanthrene in the presence of C_{60} , the phenanthrene: -dihydrophenanthrene ratio is 33, while in its absence, other conditions being equal, it is 1.3.⁴⁸ The C_{60} fullerene is then converted into reduced derivatives with different hydrogen contents. After prolonged heating, the hydrogenated fullerene derivatives are dehydrogenated, as in the case of $C_{60}H_{36}$.⁴⁵ Thus C_{60} behaves as a catalyst in this reaction.

The effect of C_{60} on the cleavage of the carbon-carbon bond in 1,2'-dinaphthylmethane has been investigated in the presence of hydrogen donors such as dihydroanthracene, dihydrophenanthrene, *etc.* (Scheme 4).⁴⁸ It was found that, when C_{60} is added to anthracene system, the rate constant of the reaction increases

appreciably and the selectivity (the 2-methylnaphthalene: 1-methylnaphthalene ratio) changes. On hydrogenolysis of 1,2'-dinaphthylmethane in the absence of fullerene, the ratio is ~1.5, whilst in the presence of fullerene-containing systems it reaches ~4.4–5.4. The results indicate the involvement of C_{60} in the acceptance of hydrogen atoms from the hydroaromatic compounds or the corresponding hydroaryl radicals and in the subsequent hydrogen transfer to 1,2'-dinaphthylmethane.

Scheme 4



Ar/ArH₂ = anthracene/9,10-dihydroanthracene, pyrene/4,5-dihdropyrene, or phenanthrene/9,10-dihydrophenanthrene.

The hydroalkylation of fullerene by unsaturated compounds, such as hept-1-ene and 4-allylanisole, with formation of fullerene alkyl hydrides, has been reported.⁴⁹

It has been observed that, when various hydrocarbons, including alkanes, are come into contact with fullerenes (fullerene cocoons)[†] at high temperatures (500–700 °C), large amounts of molecular hydrogen and of the products of the dehydrogenation of the hydrocarbons are evolved into the gas phase.⁵⁰ The reactions were carried out at a very low pressure of the hydrocarbons (1 Torr),⁵⁰ which indicates a high activity of fullerenes in the activation of C-H bonds, including the bonds in alkanes. In contrast to industrial pyrolytic processes, lower olefins predominate in the reaction products in this instance. For example, ethene, propene, and hydrogen have been obtained from hexane in the complete absence of ethane, propane, and C₄ hydrocarbons.⁵⁰ Thus, apart from the dissociation of the C-H bonds, the cracking of strong C-C bonds in alkanes also takes place effectively on the fullerene cocoons. The pyrolysis of toluene is also accompanied by the dissociation of the CH₃-C₆H₅ bond, which is indicated by the presence of methane and benzene in the reaction products.⁵⁰

The activation of methane also becomes possible in the above temperature range (the C-H bond energy is 105 kcal mol⁻¹).^{51–53} The threshold temperature of the onset of pyrolysis of methane on fullerene black[‡] as the catalyst is 600 °C, which is lower by 250 °C than the reaction threshold in the absence of a catalyst and lower by 100–200 °C than the threshold temperatures for graphite, activated charcoal, and other carbon catalysts.^{51–53} High degrees of conversion, of methane (dozens of %) are attained under the conditions of a flow reactor at temperatures above 900 °C. The dehydrogenating activity of the initial fullerene black is then so high that at the beginning of the reaction hydrogen is virtually the only gaseous product.⁵³ Only after the accumulation of a certain amount of pyrolytic carbon and the concomitant decrease in the dehydrogenating activity of the catalytic system do gaseous hydrocarbons, among which ethene predominates, appear in the products. Further accumulation of pyrolytic carbon leads to a decrease in both the degree of conversion of methane and in the selectivity with respect to ethene.⁵³ This undesirable phenomenon was overcome by diluting the initial stream of methane with hydrogen.⁵³

[†] Fullerene cocoons are polymeric structures, which are nonsublimable (in contrast to fullerenes) at high temperatures and in which the fullerene molecules are linked to one another by oxygen bridges, the number of which is approximately equal to the number of fullerene molecules.⁵⁰

[‡] Fullerene black is the finely dispersed carbon material remaining after the extraction of fullerenes with a suitable solvent from the fullerene-containing soot obtained on electric arc vaporisation of graphite under an inert gas atmosphere.

[¶] All attempts to observe the EPR spectrum of the radical-anions of the hydrogenated and deuterated fullerenes were unsuccessful.⁴⁵

It has been observed⁵³ that the addition of hydrogen to methane can alter drastically the process selectivity. At a sufficiently high dilution, the reaction begins immediately, without the induction period mentioned above, whereupon virtually pure ethene is formed (the selectivity with respect to ethene is 90%–94%) while the amount of propene does not exceed 6%–10% and there are only traces of other products.⁵³ The degree of conversion of methane is comparatively low ($\sim 4\%$), but remains stable for many hours at 1000 °C. The accumulation of pyrolytic carbon is not observed under these conditions.

Such influence of dilution on the process is fully reversible, which suggests that the mechanism of this interesting phenomenon involves the dynamic blocking by hydrogen of the most active dehydrogenation centres on the surface of fullerene black. Fullerene black consists mainly of three–five layer stacks of markedly curved graphene sheets with a local radius of curvature of the order of the dimensions of the usual fullerenes.⁵⁴ The curvature caused by the presence of five- and seven-membered rings in the structure of the sheet arises under the highly non-equilibrium conditions in the electric arc, characterised by high temperature and carbon species concentration gradients. This distinguishes fullerene black from all industrial blacks, activated charcoals, and graphite, the only basic structural element of which is absolutely planar graphene sheets, *i.e.* planar two-dimensional macromolecules consisting of carbon atoms, forming adjacent hexagons. The curvature of the carbon surface in fullerenes and in fullerene black may be the cause of their higher reactivity towards dihydrogen and C–H bonds.

The mechanism of the activation of hydrocarbons RH in the presence of fullerenes is as follows. The C–H bond is activated by the strained $C^*=C^*$ double bond of the curved carbon surface in the primary step of the interaction of the hydrocarbon with fullerene, which results in the formation of the $R-C^*-C^*-H$ fragment. The subsequent migration of hydrogen atoms and the radicals R on the surface, multiple reversible addition of the RH molecules and hydrogen, reactions of the two-centre and β -elimination types, and also the dissociation of the free radicals R and other processes possible at sufficiently high temperatures are responsible for the formation of the set of products in the liquid-phase and gas-phase reactions investigated. Thus methylated derivatives of fullerenes, namely $C_{60}(CH_3)_n$, were detected in the mass-spectrometric analysis of the fullerene-containing soot, carried out after the high-temperature dehydrogenation of methane.⁵¹ Modification of the catalyst, for example doping of the fullerene-containing soot with potassium, increases the selectivity in the formation of higher hydrocarbons from methane.⁵²

4. Reduction of fullerenes in a metal–acid system

The reduction of C_{60} in metal (M)–acid systems, where $M = Sn[E^{Ox/Red}(Sn^{2+}/Sn) = -0.75\text{ V}]$, $Fe[E^{Ox/Red}(Fe^{2+}/Fe) = -1.05\text{ V}]$, and $Zn[E^{Ox/Red}(Zn^{2+}/Zn) = -1.37\text{ V}]$, has been investigated. The potentials were measured relative to Fe^+/Fe ($Fe = \text{ferrocene}$).⁵⁵ In principle, these results make it possible to obtain the anions C_{60}^- and C_{60}^{2-} since the potentials for C_{60}^0/C_{60}^- and C_{60}^-/C_{60}^{2-} are -0.98 and -1.37 V relative to Fe^+/Fe . However, the Sn–acid and Fe–acid systems proved to be ineffective for the reduction of C_{60} and only the Zn–acid system was found to be suitable for such purposes. The acids employed are 6 M or 12 M HCl, glacial CH_3COOH , and concentrated H_2SO_4 . When a toluene solution of C_{60} is refluxed under an inert atmosphere, a mixture consisting of 7% of $C_{60}H_2$, 3% of $C_{60}H_4$, and 1% of $C_{60}H_6$ is formed. It was separated by means of HPLC. It contains also small amounts of fullerenes with a higher hydrogen content ($C_{60}H_6$ – $C_{60}H_{22}$), but these were not isolated.⁵⁵ The mass spectra of the fullerene hydrides obtained by this method demonstrate a strong tendency of the products for fragmentation back to the parent C_{60} on ionisation. It has been demonstrated that the substance with a mass of 722, present in the reaction mixture in the largest amount, has the same spectroscopic and chromatographic characteristics as 1,2- $C_{60}H_2$.³³ Thus, under the conditions indi-

cated, mainly the most stable dihydrofullerene isomer (1,2- $C_{60}H_2$) is formed in the C_{60} –Zn–acid system. Treatment of the reaction mixture obtained as a result of the interaction of C_{60} with zinc in hydrochloric acid with DDQ leads to C_{60} , which confirms the formation of hydrogenated C_{60} derivatives.

The reduction of C_{60} and C_{70} in the Zn–conc. HCl–toluene (benzene) system under an inert atmosphere takes place rapidly even at room temperature and leads to the preferential formation of $C_{60}H_{36}$, $C_{70}H_{36}$, and $C_{70}H_{38}$ in the absence of light.⁵⁶ In the case of C_{60} , appreciable amounts of more highly hydrogenated derivatives are also formed in this case: $C_{60}H_{38}$ (15%) and $C_{60}H_{40}$ (3%).⁵⁶ The C_{70} fullerene is reduced at a lower rate than C_{60} . Furthermore, the compound $C_{70}H_{36}$ is thermally less stable than $C_{60}H_{36}$.

The sensitivity of fullerene hydrides synthesised by this method to oxygen increases appreciably in solution in the presence of light. The peaks due to the initial fullerenes and their lower hydrides are therefore absent from the mass spectra of $C_{60}H_{36}$, $C_{70}H_{36}$, and $C_{70}H_{38}$, obtained with the aid of ionisation by electron impact, only in the case where the spectra have been run immediately after work up. Otherwise, peaks corresponding to completely dehydrogenated products (C_{60} and C_{70}) and the lower hydrides ($C_{60}H_{18}$ in the case of $C_{60}H_{36}$), as well as fullerols appear in the mass spectra. The formation of highly hydrogenated fullerenes, including $C_{60}D_{44}$ and $C_{70}D_{48}$ on treatment with Zn in concentrated DCl, is associated with the greater stability of the C–D bonds compared with the C–H bonds, as a result of which the loss of the resonance energy of the initial fullerene is partly compensated. The hydrogen atoms in fullerene hydrides do not undergo H/D exchange in the absence of light either with D_2O , or with $D_2O/NaHCO_3$, or with $D_2O/NaOH$, which indicates a decrease in the acidity of the C–H bond in $C_{60}H_{36}$ compared with, for example, the acidity of this bond in the adduct of C_{60} with morpholine $[NH(CH_2)_4O]$ having the composition $HC_{60}N(CH_2)_4O$ since in the latter case hydrogen rapidly exchanges with CH_3OD .^{5,57}

The hydrides $C_{60}H_{36}$ and $C_{70}H_{36}$ are resistant to further reduction by hydrogen in the presence of the Rh/ Al_2O_3 catalyst (toluene is used as the solvent), but they tend to form trimethylene adducts (this is indicated by the appearance in the mass spectrum of peaks with m/z 798, 840, and 882 in the case of $C_{60}H_{36}$) via an unknown mechanism.⁵⁶ When the reaction was carried out in benzene- d_6 (as a solvent), H/D exchange between the fullerene hydride and the deuterium of the solvent was observed.⁵⁶

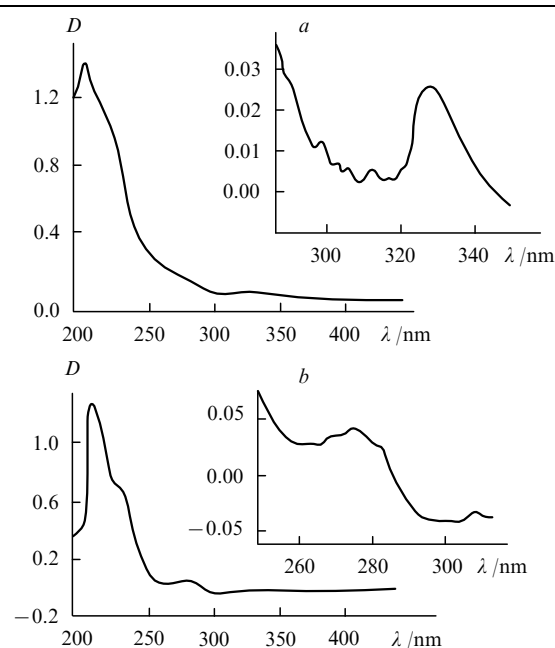


Figure 3. Absorption spectra of $C_{60}H_{36}$ (a) and $C_{70}H_{36}$ (b) (higher hydrides are present as impurities).⁵⁶

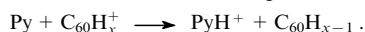
The UV spectrum of $C_{70}H_{36}$ has a broad band with a maximum at 275 nm and a shoulder at 223.5 nm (Fig. 3), which are close to the wavelengths λ for naphthalene (221 and 258–280 nm).⁵⁶ According to the authors,⁵⁶ this is consistent with the aromatic structure proposed for $C_{70}H_{36}$.⁵⁸

5. Reduction of fullerenes by hydrogen

The direct reduction of C_{60} and C_{70} has been carried out in the solid phase at a hydrogen pressure of 50–80 MPa and a temperature of 573–623 K without using a catalyst.⁵⁹ Fullerene hydrides having the composition $C_{60}H_x$ ($x = 2–18$) and $C_{70}H_y$ ($y = 4–30$), identified with the aid of mass spectrometry, are then formed. The authors⁵⁹ also attempted to answer the question whether hydrogen atoms or molecules can be added at a high pressure and an elevated temperature to endohedral positions in the fullerene molecule. In order to avoid losses of fullerene, the reaction was carried out in a sealed capsule. The material of the capsule (25% Ag–75% Pd alloy, Au, or glass), in which the hydrogenation is carried out, does not affect the yield of the products and the rate of hydrogenation. This provided grounds for the assumption that the hydrogenation proceeds only under the influence of hydrogen and is initiated by small amounts of atomic hydrogen, which is generated in the reaction medium at these temperatures and pressures.

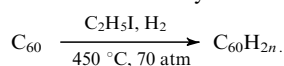
Heating of the C_{60} fullerene in a sealed AgPd capsule in a H_2 atmosphere at a temperature ≥ 950 K leads to the complete disappearance of the specimen. Since neither C_{60} nor its hydrides can diffuse from the capsule, under the given experimental conditions fullerene apparently decomposes to low-molecular-mass fragments, which react with the material of the capsule and the presence of hydrogen then plays an important role.

The study of the products of the direct hydrogenation of fullerene showed that hydrogen usually if not always adds exohedrally to the fullerene skeleton. In order to demonstrate this fact, use was made of the proton transfer reaction



Pyridine (Py, proton affinity 220.4 kcal mol⁻¹) is a stronger base than C_{60} (proton affinity 205 kcal mol⁻¹), so that the interaction can occur only when all or some of the hydrogen atoms in the fullerene hydride are bound exohedrally, although the possibility of the endohedral binding of hydrogen is also not ruled out. Hydrogenation lowers somewhat the ionisation potential of fullerene: $I(C_{60}H_x = 2–18) \leq 7.53$ eV, while $I(C_{60}) = 7.6$ eV. It has been noted that the hydride $C_{60}H_x$, obtained by direct solid-phase hydrogenation is distinguished by a greater stability than the specimens obtained by other methods.^{29, 60}

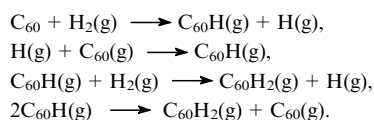
Fullerite⁸ (a mixture of C_{60} and C_{70}) was hydrogenated (~ 1 h) by hydrogen at 400 °C and a H_2 pressure of 6.9 MPa using ethyl iodide as the promoter of the formation of atomic hydrogen in the system.⁶¹ In the absence of C_2H_5I , hydrogenation does not occur. An increase in temperature and pressure leads to a decrease in the degree of hydrogenation. Mass-spectrometric analysis of the reduced fullerite by FAB-MS technique showed that a mixture of hydrides $C_{60}H_{36}$ and $C_{70}H_{36}$ is mainly formed in the reaction. The use of 'harder' mass-spectrometric methods, such as EI and LD, proved impossible owing to the thermal decomposition of the product to compounds with lower molecular masses ($C_{60}H_{18}$, $C_{60}H_8$, etc. in the case of $C_{60}H_{36}$). No spectroscopic evidence for the ethylation or iodination of fullerene under these conditions was found. The reaction product is insoluble in the majority of organic solvents and is only slightly soluble in nitrobenzene, which distinguishes it from the hydride obtained by Birch reduction²⁹ or by the transfer hydrogenation.⁴⁵



§ The solid crystalline material consisting of pure fullerenes or their mixtures is called fullerite.

The solid-phase ^{13}C NMR spectrum of polyhydrogenated fullerene $C_{60}H_{36}$, obtained by radical hydrogenation, indicates the presence of a single highly symmetrical compound, possibly of D_{3d} or C_{3i} symmetry.⁶¹ On the other hand, Buhl *et al.*⁶² see no agreement between the experimental ^{13}C NMR spectrum of $C_{60}H_{36}$ ⁶¹ and the D_{3d} structure.

The reaction of C_{60} (up to 90% in the mixture) with an ultrasonic molecular beam of H_2 or D_2 has been investigated at 540–750 °C and a pressure of 100–500 Torr.⁶³ It was found that the interaction of H_2 with C_{60} under these conditions leads to both the hydrogenation of fullerene (up to eight hydrogen atoms may add to C_{60}) and to the formation of low-molecular-mass hydrocarbon species as a consequence of the disruption of the C_{60} skeleton. When H_2 is replaced by D_2 , a large isotope effect is observed. The main product is $C_{60}H_2$, the yield of which depends both on the H_2 pressure and on the temperature.



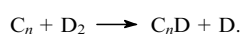
Solid C_{60} has been hydrogenated by atomic hydrogen at 77 K (in a cyclohexane matrix).⁶⁴ The $C_{60}H$ ($g = 2.00218 \pm 0.0004$), $C_{60}H_{2n+1}$, and $C_{60}H_{2n}$ species were identified by EPR and IR spectroscopy and FAB-MS technique.

The hydrogenation of thin C_{60} films by atomic hydrogen has been investigated with the aid of the plasma desorption method.⁶⁵ The approach proposed⁶⁵ makes it possible to determine the degree of hydrogenation of C_{60} molecules. It was found that hydrogen is bound covalently to the fullerene molecule with formation of the hydride $C_{60}H_n$ ($n = 2–24$). The authors rule out the possibility of the formation of fullerene hydrides by the interaction of C_{60} with the residual toluene in the film under the conditions of the mass-spectrometric analysis.

An attempt to implant a hydrogen atom inside the C_{60} molecule has been reported [plasma, 10–25 eV, 550–600 °C, $(5–10) \times 10^{-4}$ Torr]. It has been shown with the aid of HPLC, ^1H NMR, and mass spectrometry that hydrogen adds exohedrally with formation of the compounds $C_{60}H_2$ and $C_{60}H_4$. No evidence has been obtained for the formation of complexes with endohedrally bound hydrogen under these conditions.⁶⁶

We may note that the addition of a H atom to C_{60}^+ in the gas phase takes place very effectively, the bimolecular reaction rate constant being $k \approx 6 \times 10^{13}$ cm³ mol⁻¹ s⁻¹ at 294 K and a helium pressure of 0.4 Torr.⁶⁷ Under the same conditions, the reaction of C_{60}^+ with molecular hydrogen does not occur,⁶⁸ but a C_{60} ion accelerated up to an energy of 5–6 keV is apparently capable of incorporating a H_2 molecule into the carbon framework with formation of the endohedral complex $H_2@C_{60}^+$.⁶⁹

The hydrogenation of the molecules of fullerenes and other neutral C_n carbon clusters in the gas phase at a high temperature has been investigated by the TOF-MS technique with LD evaporation of the test substance for the wide range $n = 6–75$.⁷⁰ The clusters were obtained by the laser pulse evaporation of graphite and were mixed with D_2 in a flow reactor. The kinetics of the variation of the C_n concentrations and of the formation of the C_nD_m products ($m = 1–4$) have been investigated. Deuterated clusters are formed as a result of the successive addition of D atoms via the reaction involving direct abstraction from the D_2 molecule ($k \approx 10^{11}$ cm³ mol⁻¹ s⁻¹ at 2800 K).



In certain cases, excited C_nD^* species undergo unimolecular decomposition with the preferential formation of the compound $C_3(p = 3)$:



In the case of 'even' C_{2n} clusters with $n < 20$, the reaction product $C_{2n}D_2$ is a linear polyyne (a carbyne), which is inert in relation to more extensive hydrogenation. An attempt may be

made to use this fact in order to obtain the crystalline form of the carbyne by depositing on a cold support the products of the reaction of graphite vaporised in a hydrogen atmosphere. The possibility of the existence of such a form of the carbyne stable at room temperature is indicated by experiments on the condensation of the products of the electric spark disintegration of graphite on a copper plate under an argon atmosphere (0.5 Torr)⁷¹ and also by the presence of linear carbon molecules in the fullerene black obtained by the electric arc⁷² or laser⁷³ vaporisation of graphite.

The 'odd' C_{2n+1} clusters react with D_2 at a higher rate than the 'even' clusters.⁷⁰ This difference increases progressively with increase in n in the fullerene mass range ($n > 36$), where the reactivity of even clusters (fullerenes) diminishes and that of the odd clusters (structures with open carbon shells of a radical character with a larger geometrical collision cross-section) increases.⁷⁰

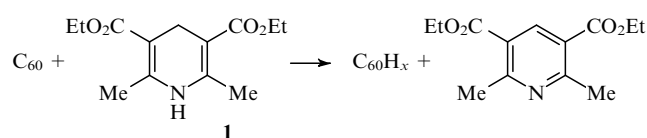
The high-temperature hydrogenation reactions of fullerenes and their precursors influence the yield of fullerenes in hydrocarbon flames and in a carbon arc. Even several per cent of hydrogen in helium fully blocks the formation of C_{60} in the electric arc vaporisation of graphite.⁷⁴ The possibility of the formation of the hydrides $C_{60}H_x$ in this process for a low hydrogen content in the gaseous medium has not been specially investigated. On the other hand, under a hydrogen atmosphere, open carbon nanotubes appear in the cathodic deposit formed in a d.c. carbon arc.^{75,76} Under these conditions, the inner channel of the open nanotubes is free of the amorphous carbon deposits characteristic of tubes opened by treatment with strong oxidants. In addition, the number of spherical carbon nanoparticles in the deposit decreases sharply under a hydrogen atmosphere.^{75–77} Thus the use of hydrogen is extremely promising for the solution of the problem of the preparation of open and pure nanotubes. The effect of hydrogen consists in this instance of the hydrogenation of the end-face of the growing open nanotube with formation of relatively stable C–H bonds, which prevent the formation of five-membered rings and hence the closure of the tube when the temperature is reduced.^{75,76}

6. Reduction of fullerenes by organic compounds under irradiation

In the study by the EPR method of the products formed in the photolysis (high-pressure Hg/Xe lamp) of a benzene solution of C_{60} containing thiophenol, cyclohexa-1,4-diene, or Bu_3SnH , it was found that the EPR spectrum consists of two lines with a splitting of 33 G.⁷⁸ The authors assigned this spectrum to the radical $C_{60}H^\bullet$ — the initial product of the reaction of the photogenerated hydrogen atom with C_{60} (the hydrogen atoms are formed on photolysis of thiols, tin hydrides, and cyclohexa-1,4-diene).

On heating (100 °C, toluene) or flash photolysis (Nd^{3+} : YAG-laser, $\lambda = 532$ nm, benzonitrile) of the C_{60} fullerene–diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**1**) reaction mixture, appreciable changes are observed in the absorption spectrum of C_{60} in the visible region: bands at 434 and 708 nm, characteristic of dihydrofullerene, appear in it, while the bands characteristic of free C_{60} vanish. It has been shown by ^1H NMR that the solution contains the diethyl ester of 2,6-dimethylpyridine-3,5-dicarboxylic acid — the product of the dehydrogenation of compound **1**. The formation of the hydrides $C_{60}H_x$ ($x = 2, 4, 6$) has been demonstrated mass-spectrometrically.⁷⁹

Scheme 5



7. Catalytic hydrogenation of fullerenes

The possibility of the catalytic hydrogenation of C_{60} in the presence of transition metals has been investigated.^{80–85} It was found that, in the presence of Ru/C, Pt/C, and Pd/C, fullerene is

hydrogenated (H_2 pressure 100 atm, 180 °C), affording a low yield of $C_{60}H_{36}$ (a mixture of $C_{60}H_{36}$ and $C_{60}H_{18}$ is formed depending on the hydrogen pressure). The activity of the catalysts varies in the sequence $Pt < Ni < Pd < Ru$. The low yield of the hydrogenated products is due to a number of causes, including the high adsorption capacity of the activated charcoal, which leads to losses of fullerene and its hydrides, and also to the hydrogenation of the solvent (toluene) on certain catalysts (Ru/C, Ni/diatomite). The formation of C_{60} complexes with palladium, stable up to 120 °C (their dissociation begins above this temperature), has been reported.⁸⁶ This is in fact the temperature of the onset of the hydrogenation of C_{60} in the presence of Pd/C.^{80,81} The fullerene hydrides formed are unstable even under an inert atmosphere.

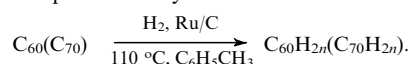
The hydrogenation of C_{60} has been investigated in C_6D_6 in the presence of Rh/ Al_2O_3 .⁸⁷ Comparison of the ^1H and ^{13}C NMR spectra of the product and of $C_{60}H_2$ synthesised by the method described by Henderson and Cahill³³ demonstrated their complete identity. It was found that the yield of $C_{60}H_2$ in the hydrogenation of C_{60} in the presence of Rh/ Al_2O_3 initially rose, reaching ~14%, and then diminished, the yield of the more highly hydrogenated fullerenes increasing under these conditions (HPLC data). The reaction product was fairly stable in the reaction medium, but it decomposed in the light on treatment with O_2 and was partly converted into C_{60} .

The reactivity of the coordinated C_{60} fullerene has been demonstrated in relation to the hydrogenation in the solid phase of the palladium fulleride $C_{60}Pd_{4.9}$ by molecular deuterium (473–673 K, D_2 pressure 20 atm).⁸⁸ In the course of the reaction under relatively mild conditions, a set of deuterofullerenes $C_{60}D_x$ ($x = 2–26$) are formed, the main products being those with $x = 2, 4, 18$, and 26. Deuterofullerenes containing an odd number of deuterium atoms have also been detected by means of field desorption (FD-MS) mass spectrometry. The IR spectrum of the fullerene deuteride obtained at 473 K contains a broad band with the centre at 2150 cm^{-1} [$\nu(C-D)$], the intensity of which increases with increase in the reaction temperature. The spectrum of a solution of the fullerene deuteration product in the visible range contains bands at 407(C_{60}), 435, and 715 nm.

The direct solid-phase synthesis of $C_{60}H_2$ from C_{60} and the stoichiometrically controlled amount of hydrogen has been achieved (reaction temperature 400–500 °C, reaction time 12 h).⁸⁹ Palladium hydride was used as the source of activated hydrogen. The main product is 1,2- $C_{60}H_2$ (~15%). $C_{60}H_4$ is also formed in a small amount (3%–5%) in the form of the thermodynamically most stable 1,2,3,4- $C_{60}H_4$. The isomerisation of the fullerene hydrides $C_{70}H_2$ and $C_{60}H_4$ to the most stable 1,2- and 1,2,3,4-isomers had already been observed.^{42,43} With increase in the hydrogen pressure, the yield of $C_{60}H_4$ rises, while the amount of dihydrofullerene remains unchanged.

The catalytic hydrogenation of C_{60} in boiling toluene in the presence of Ru/C leads to highly hydrogenated compounds (up to $C_{60}H_{50}$).⁸³ The degree of hydrogenation increases with increase in the hydrogen pressure and reaction temperature. The signal, corresponding to the ion with m/z 780, which belongs according to the authors,⁸³ to the hydride $C_{60}H_{60}$, has been detected in the mass spectrum (FD-MS) of the C_{60} hydrogenation products obtained at 280 °C and a H_2 pressure of ~130 atm.

In boiling toluene, the fullerene hydrides $C_{60}H_{18}$, $C_{60}H_{36}$, $C_{60}H_{40}$ are dehydrogenated by DDQ, the yields of C_{60} being 51%, 48%, and 45% respectively.⁸² The hydrogenation of C_{70} under similar conditions (Ru/C catalyst) leads to $C_{70}H_{36}$.⁸⁴ The dehydrogenation of the latter with the aid of DDQ also proceeds almost quantitatively.



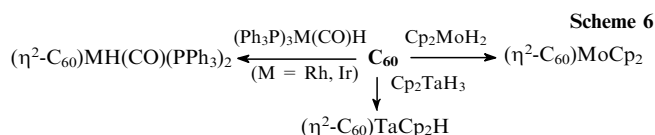
The dehydrogenation of the hydrofullerenes $C_{60}H_{2n}$ and $C_{70}H_{2n}$ on treatment with DDQ in the presence of catalysts (Ru/C) or on heating has also been investigated.⁸⁵ High yields of fullerenes are obtained only in the presence of DDQ as the dehydrogenating

agent, whereas refluxing of $C_{60}H_{36}$ in toluene in the presence of Ru/C leads to the appearance of only 1% of C_{60} (FD-MS).

It has been found that the temperatures corresponding to the loss of 1% of mass for $C_{60}H_{18}$ and $C_{60}H_{36}$ are 164 and 175 °C (in a nitrogen atmosphere) and 348 and 247 °C (in air) respectively. The degrees of conversion of $C_{60}H_{18}$ and $C_{60}H_{36}$ in nitrogen at 600 °C are 30.5% and 26.8%, whereas at 400 °C in air the corresponding values are 56.6% and 40.1%.⁸⁵

8. Interaction of fullerenes with transition metal hydride complexes

Treatment of solutions of C_{60} (C_{70}) in toluene, benzene, or CH_2Cl_2 with metal (Ir, Rh, *etc.*) hydride complexes at room temperature leads to an instantaneous change of the colour of the solution. Three bands then appear in the electronic spectra of the solutions at $\lambda = 435, 604(600),$ and $640(630)$ nm. Their intensity is significantly higher than the intensity of the absorption of fullerenes in this region, which indicates the quantitative formation of metal complexes with fullerene (Scheme 6). The latter were characterised by a spectroscopic method.^{90–93} The molecular and crystal structures of the complex $\eta^2-C_{60}Rh(CO)H(PPh_3)_2$ have been determined.⁹³ The composition of the complexes $(\eta^2-C_n)IrH.(CO)(PPh_3)_2$ ($n = 60, 70$), their configuration, and the position in the fullerene nucleus of the $C=C$ double bond coordinated to the metal were established from the IR spectra (by comparative analysis relative to the spectra of the corresponding deuterated analogues) and ^1H and ^{31}P NMR spectroscopic data.⁹¹



The complexes $(\eta^2-C_{60})TaCp_2H$ and $(\eta^2-C_{60})MoCp_2$ are formed on interaction of the hydride complexes Cp_2TaH_3 and Cp_2MoH_2 with fullerene. Molecular hydrogen is apparently evolved as a result of the reaction, but its presence in the gas phase has not been demonstrated.⁹⁰ The interaction of the 16-electron square planar complex $PtHCl(PPh_3)_2$ and of the 18-electron octahedral complex $Ir(H)_2Cl(CO)(PPh_3)_2$ with the C_{60} fullerene on refluxing an alkaline (NaOH) solution of the reactants in a 1 : 2 ethanol–benzene mixture leads to the formation of $(\eta^2-C_{60})Pt(PPh_3)_2$ and $(\eta^2-C_{60})IrH(CO)(PPh_3)_2$ respectively.⁹⁴

9. Hydrogenation of mechanical mixtures of powdered fullerite and hydrogen-sorbing metals and intermetallic compounds

The study of the hydrogenation and dehydrogenation reactions of fullerenes is of interest both from the standpoint of the development of systems for the accumulation and storage of hydrogen and from the standpoint of other practical applications.^{3, 28, 95, 96} Such systems are constructed nowadays on the basis of intermetallic compounds or metals capable of absorbing considerable amounts of hydrogen selectively and reversibly.⁹⁷ In this respect, fullerene hydrides which have a low density and are capable of containing up to 8 mass% of hydrogen (as in the $C_{60}H_{60}$ hydride), are of special interest. However, direct noncatalytic hydrogenation of the C_{60} fullerene proceeds effectively only at high pressures (50–85 MPa) and temperatures (573–623 K).⁵⁹ The other methods of synthesis of fullerene hydrides listed above considered as systems for the reversible storage of hydrogen have also proved to be relatively unattractive owing to the difficulty of achieving multiple repetition of the ‘hydrogenation–dehydrogenation’ cycle in the presence of solvents in the system. This difficulty can be overcome by developing processes for the solid-phase catalytic hydrogenation of fullerenes. The choice of hydrogen-sorbing intermetallic compounds and metals as potential catalysts of such processes is natural because hydrogen possesses a high chemical reactivity at the instant of its evolution from metal hydrides.⁹⁸

The reactions involving the hydrogenation of fullerenes by molecular hydrogen in the solid phase in the presence of intermetallic compounds and metals effectively sorbing hydrogen have been achieved in relation to the compounds $LaNi_5$, $LaNi_{4.65}Mn_{0.35}$, $CeCo_3$, metallic palladium and vanadium, and also the hydrides of the above compounds.^{99–101} The use of hydrides as the initial components of mechanical mixtures with fullerenes is preferable, because, owing to the high brittleness of the hydrides, the preparation of smaller particles is ensured when mixtures are treated in a vibromill compared with powdered metals and intermetallic compounds. When hydrides are used, it is possible to avoid the undesirable oxidation of the surface of the particles in the course of the mechanical milling of their mixture with fullerite powder (such milling is necessary to ensure the homogeneity of the mixture and to increase the surface of contact of the two initial components).^{99–101}

The hydrogenation of fullerenes in such mechanical mixtures proceeds quite effectively already at a hydrogen pressure of 1–2.5 MPa and temperatures in the range 573–673 K, which is indicated, for example, by the appearance in the IR spectra of the product (after the treatment of the mixtures with deuterium under these conditions)^{99–103} of an intense absorption band at 2120 cm^{-1} (stretching vibrations of the $C-D$ bonds).⁸⁸ According to the results of chemical analysis, the deuterium content in the mixture specimens increases monotonically with increase in the deuteration temperature to 673 K, with increase in the D_2 pressure, and with increase in the number of ‘ D_2 sorption-desorption’ cycles. The product with the highest deuterium content (24–26 deuterium atoms per C_{60} fullerene molecule) has been obtained in the interaction of D_2 with mixtures of fullerite and intermetallic compounds or metals at a gas pressure of 2.5 MPa and for a sevenfold repetition of the ‘heating to 673 K (1 h)–cooling to 293 K (1 h)’ cycle.^{99–101} Hydrides of similar composition are formed also when the usual hydrogen is employed.

It has been found with the aid of differential thermal analysis (DTA) and thermogravimetry of the hydrogenated mechanical mixtures that the endothermic decomposition of the fullerene hydride takes place in all cases at 800 K with evolution of 1 mass %–3 mass % of gaseous hydrogen. The constancy of the decomposition temperature (800 K) means that the presence of metals and intermetallic compounds does not affect the dehydrogenation of fullerene hydrides, in contrast to the hydrogenation process, which is appreciably facilitated in the presence of these mechanical mixtures (a decrease in hydrogen pressure from 50–80 to 1–2.5 MPa). This may be induced by the irreversible transfer of activated hydrogen from the metal to the $C=C$ bonds of the fullerene component of the mixture. It is known that the effective action of the composite system requires, apart from fine mechanical milling of the mixture in a vibromill ensuring a high area contact of the components, also several ‘hydrogenation–dehydrogenation’ cycles, during which the molecular structure of the contact apparently changes with removal of surface oxygen and the probable formation of $M-C$ bonds. The irreversible hydrogen transfer from the metal to the $C-C$ bond apparently actually occurs with participation of $M-C$ bridges. At 800 K fullerenes are effectively dehydrogenated, the $M-C$ bonds are to a large extent dissociated, preventing the reverse hydrogen transfer to the metal, whereupon the organic subsystem must evolve the excess hydrogen spontaneously without the participation of the metals.

The hydrogenated specimens of the mechanical mixtures contain, apart from fullerene hydrides, also the hydride phases of the corresponding intermetallic compounds or metals,^{99–101} which is indicated by clearly distinguishable endothermic effects in the range 350–600 K. The decomposition of the corresponding hydrides of palladium (360 K)⁹⁹ and vanadium (450 and 550 K) and of the hydride phases of the intermetallic compounds $LaNi_{4.65}Mn_{0.35}H_x$ and $CeCo_3H$ (500–600 K), accompanied by the evolution of hydrogen, takes place at these temperatures.^{100, 101} The amount of evolved hydrogen is correlated with the content of the metal or the intermetallic compound in the

composite mixture and is usually 70%–90% of the amount of hydrogen in the fully saturated stoichiometric hydrides.

Intense exothermic peaks unaccompanied by a change in the mass of the specimen have been observed on the DTA curves in the temperature range 950–1000 K for all the hydrogenated compositions (except the palladium ones) investigated.^{99–101} Their appearance is associated with the irreversible chemical interaction of fullerenes with intermetallic compounds or metals, leading to the formation of metal carbides. In the hydrogenation in the presence of vanadium, the endothermic effect observed at 900 K is due to the decomposition of fullerenes and the formation of the vanadium carbide $\text{VC}_{0.8}$ with a NaCl type lattice.¹⁰¹ In the case of compositions based on fullerite and the intermetallic compounds LaNi_5 , $\text{LaNi}_{4.65}\text{Mn}_{0.35}$, and CeCo_3 , the products of the high-temperature heating of the hydrogenated specimens are the hydrides of the lanthanide and the metallic phases of the corresponding transition metal.¹⁰⁰

In the case of palladium, the high-temperature exothermic effect is not observed and the initial phase state of the metal does not change.⁹⁹ Bands characteristic of fullerenes are retained in the IR spectra of specimens of the mixed palladium compositions heated to 1200 K, in contrast to the compositions based on vanadium, for which analogous heat treatment leads to the complete disappearance of the fullerene bands. The palladium compositions partly dissolve in toluene, in contrast to the insoluble vanadium compositions.

The absorption bands due to fullerenes are absent from the IR spectra of specimens based on intermetallic compounds heated to 1200 K, while peaks due to the metallic nickel, manganese, or cobalt phase respectively can be seen on the X-ray diffractograms. Magnetic measurements have shown that the content of ferromagnetic nickel and cobalt particles in the products of the heat treatment at 1200 K is approximately equal to the amount of Ni and Co in the initial intermetallic compounds, which indicates the almost complete decomposition of the latter. This finding and the decomposition of the fullerenes mentioned above suggest that the lanthanide metal remains in the specimen in the form of the X-ray-amorphous carbide. The chemical interaction of intermetallic compounds and fullerenes proceeds after the completion of the decomposition of the fullerene hydrides, which apparently facilitates the formation of carbides as a result of the removal of the impurity oxygen (there is also a possibility of the preliminary formation of a small number of metal–carbon bonds).

Thus the presence of carbide-forming metals (including those in the intermetallic compounds) in the compositions leads to the degradation of the fullerene structures even when the temperature corresponding to the complete evolution of hydrogen from the hydrogenated composites (800 K) is only slightly exceeded. The formation of metal carbides and metallic phases observed under these conditions lowers the capacity of the composites with respect to hydrogen and the sorption–desorption reversibility. The elimination of this effect, which is undesirable for hydrogen storage systems, may involve the determination of the upper permissible limiting temperature to which the composite material may be heated and also the search for materials for which the formation of carbides is difficult or impossible.¹⁰¹

One of the most significant obstacles on the way to the technical realisation of fullerene-based hydrogen accumulators is the evolution of a large amount of heat in the adsorption of hydrogen by compacted fullerite,²⁸ which, when combined with the low thermal conductivity of the latter, leads to its mechanical disintegration and also to the retardation of the saturation by hydrogen and failure of the latter to reach completion. The use of compacted mixed compositions of hydrogen-sorbing metals or intermetallic compounds with fullerites makes it possible to deal with this problem. Other advantages of mixed compositions is significant softening of the conditions governing the hydrogenation of the double bonds of the fullerene molecules, the possibility of the multiple repetition of the ‘hydrogenation–dehydrogenation’ cycle, and the ability of the hydrogenation catalyst to

absorb hydrogen. All these factors make the mixtures examined above promising for practical applications.

III. Properties of fullerene hydrides

1. The stability of fullerene hydrides

From the very beginning of the studies on fullerenes, chemists endeavoured to obtain the fully hydrogenated $\text{C}_{60}\text{H}_{60}$ molecule, but this has not been achieved hitherto.^{29, 45, 56, 80–85} As a rule, mixtures of fullerene hydrides are obtained in all the experiments and the main products are usually $\text{C}_{60}\text{H}_{36}$ and $\text{C}_{70}\text{H}_{36}$. These polyhydrofullerenes are the most stable also according to theoretical calculations.^{47, 58, 102–106} However, even these decompose slowly in solution, which hinders their detailed investigation by spectroscopic methods.^{45, 56, 107} Even solid specimens of fullerene hydrides having the same empirical formula but synthesised by different methods exhibit markedly different solubilities, resistances to the action of light and air, capacities for prolonged storage, and other properties,^{29, 45, 59, 61, 80–85} which is apparently induced both by the structural differences between the polyhydrofullerenes themselves and by the presence in the composition of the solid fullerene hydride specimens of different amounts of crystallisation solvents and impurities comprising the components of the catalytic hydrogenation systems, as well as the presence of inhomogeneities and defects in the molecular structure. TGA and emission IR spectroscopy have shown that the fullerene hydrides obtained under the conditions of radical hydrogenation begin to decompose at 350 °C,⁶¹ while the $\text{C}_{60}\text{H}_{36}$ specimen obtained by Birch reduction²⁹ began to darken already at 170 °C.

The causes leading to instability of the hydrofullerenes^{38, 40, 45, 56} may also be the strain in the newly formed ring as a result of the breakdown of the sp^3 hybridisation of the carbon atoms, the appearance of 5–6 double bonds (Fig. 4), and the steric influence of the hydrogen atoms on one another when their number is large.

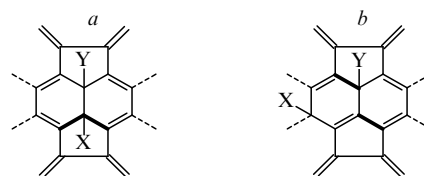


Figure 4. The 1,2- (a) and 1,4-addition (b) of XY to fullerene.

The instability of $\text{C}_{60}\text{H}_{60}$ should be associated principally with the deviation of the configuration of the bonds between the carbon atoms from the regular tetrahedral configuration. In this molecule, there are 20 sterically strained cyclohexane fragments on the surface of the sphere. According to the results of molecular-mechanical calculations, the strain may be reduced if at least ten hydrogen atoms in the $\text{C}_{60}\text{H}_{60}$ molecule are attached exohedrally. This is the most stable conformation for $\text{C}_{60}\text{H}_{60}$.¹⁰⁸ The difference between the energies of this conformer and the compound in which all the hydrogen atoms are attached exohedrally is 400 kcal mol^{−1}.

The preferred paths in the fullerene halogenation and hydrogenation reactions have been analysed theoretically.¹⁰⁹ Electronic effects are more significant in the interaction of fullerene with fluorine; fluorine adds preferentially in the *ortho*-positions in the 5–6 or 6–6 bonds, although according to theoretical analysis 1,4-addition (Fig. 4) is also possible. On the other hand, in the interaction of C_{60} with bromine the most stable isomer is formed as a result of 1,4-addition and the direction of the fullerene hydrogenation reaction is intermediate between the directions of the reactions with fluorine and bromine.

2. The state of hydrogen in solid fullerene hydrides

In the direct synthesis of solid fullerene hydrides under a high pressure of hydrogen in the absence of solvents and catalysts, the

formation of the most stable specimens is ensured.^{59,110} Such specimens are most suitable for the study of the nature of the binding of hydrogen by fullerenes in the solid phase. The interest in this problem has been stimulated by the possibility of encapsulating hydrogen molecules either in the intermolecular cavities of the crystal structure of fullerene hydrides or inside the polyhydride carbon framework. These hypotheses are confirmed by the experimental observations made by the investigators of the MER Corporation (USA). The electrochemical cathodic saturation of the C₆₀ fullerite with hydrogen results in the formation of compounds containing between 24 and 56 hydrogen atoms per C₆₀ molecule and part of this hydrogen is not bound covalently and is readily removed. The conjugation of the double bonds in the fullerene molecule is then retained even for the empirical composition C₆₀H₅₆.²⁸ The synthesis of compounds having the superstoichiometric composition C₆₀H_{60+x} (x reaches 24) by the hydrogenation of fullerite in the region of moderately high temperatures and hydrogen pressures has been reported (without experimental details), the integrity of the carbon framework of the fullerene molecule being retained in these compounds.¹¹¹ This intriguing result may imply that under the reaction conditions hydrogen molecules may permeate through the cyclohexane fragments of the shell of the perhydrogenated C₆₀H₆₀ fullerene into its inner cavity and may accumulate in the latter. This possibility merits detailed study.

Treatment of C₆₀ fullerite with hydrogen (PH = 14 MPa) at room temperature leads only to the formation of an interstitial solid solution of molecular hydrogen, *i.e.* a compound in which the type of packing of the fullerene molecules in the crystal remains unchanged on slight alteration of the lattice parameters.¹¹² The formation of C–H bonds or new interstitial phases with an altered (compared with the initial fullerite) type of packing of the C₆₀ molecules is not observed under these conditions.

In the analogous direct noncatalytic solid-phase synthesis at 600 K, hydrogen actively interacts with C₆₀, giving rise to the hydrides C₆₀H _{x} = 50–8 MPa)⁵⁹ and $x \approx 23$ (at P_{H_2} = 0.6 GPa).¹¹⁰ The hydrides obtained in this way can be stored for a long time without a significant change in composition and properties. The pressures employed in the above studies^{59,110} did not exceed the threshold value of 0.7 GPa at which the bulk–phase polymerisation of C₆₀ fullerene begins at 600 K with formation of C–C bonds between neighbouring fullerene molecules.¹¹³ The temperature of the synthesis was also lower than the initial 950–1000 K level of the temperature range corresponding to the irreversible degradation of fullerene hydrides obtained by different methods.^{59,110} The integrity of the fullerene molecules in the hydrogenated specimens was achieved thereby.¹¹⁰ The hydrogen content in such specimens is relatively low,^{59,110} but the possibilities for its increase whilst retaining the integrity of the carbon framework of C₆₀ have not been fully exhausted.

An attempt has been made¹¹⁰ to establish the state of hydrogen in fullerene hydride. For this purpose, the chamber with the specimen was cooled after the high-temperature treatment at a high hydrogen pressure¹¹⁰ and the specimen was extracted directly into liquid nitrogen. The ‘quenched’ specimen was then heated in a calibrated evacuated space up to 300 K, whereupon the evolution of 2.8 hydrogen atoms per C₆₀ molecule was observed. The ‘annealed’ specimen obtained in this way contained about 23 atoms of covalently bound hydrogen per C₆₀ molecule.

Crystallographic data indicate the same type of packing (a body-centred cubic lattice) of the C₆₀ molecules in the quenched and annealed specimens. The volume per C₆₀H _{x} molecule in the annealed specimen is then smaller by 61 Å³ than in the quenched specimen. Thus the specific volume of the hydrogen evolved on annealing was 61/2.8 $\approx$ 22 Å³ per H atom, which is close to the specific volume of solid molecular hydrogen at 4.5 K (19.022 Å³ per H atom). This fact shows that the hydrogen evolved was present in the quenched specimen in the form of hydrogen molecules occupying the interstitial cavities in the C₆₀H _{x} lattice. There is evidence that these are not octahedral but tetrahedral interstices in the body-centred cubic lattice.¹¹⁰

The state of hydrogen in fullerene hydrides has also been investigated by nonelastic neutron scattering spectroscopic methods.¹¹⁰ The rotational spectrum of the hydrogen molecules inserted in the interstices obtained at 85 K¹¹⁰ contains distinct absorption bands corresponding to transitions with the 0 $\rightarrow$ 1, 1 $\rightarrow$ 2, and 0 $\rightarrow$ 2 changes in the rotational quantum number. Thus the inserted hydrogen molecules exist as both para-hydrogen and ortho-hydrogen (at 85 K, their equilibrium ratio is 85:15). The rotational spectra of the interstitial hydrogen differ somewhat from those of the free molecules, which is a consequence of the interaction of the hydrogen rotator with the C₆₀H _{x} ($x \approx 23$) molecules surrounding the cavity. There are similar differences in the rotational spectrum of the molecular hydrogen trapped in amorphous carbon.^{114,115} However, in the latter case, the rotational bands are broader, which apparently indicates the presence of a set of sites where hydrogen molecules are located with different potentials of the interaction with the rotator. On the other hand, in the solid fullerene hydride C₆₀H _{x} (H₂)_{1.4} ($x \approx 23$) there is apparently one such site.

The vibrations in the low-frequency part of the spectrum (from 0 to 65 cm^{−1}) correspond to the intermolecular interaction in C₆₀H _{x} ($x \approx 23$).¹¹⁰ Certain differences in the intermolecular vibrational spectra in solid C₆₀H _{x} ($x \approx 23$) and C₆₀ have been noted. They are due to the anisotropy of the moment of inertia of the C₆₀H _{x} molecules, leading to the splitting of the libration bands, and also to the much higher dispersion of the libration modes of the hydrogenated C₆₀ compared with pure C₆₀. However, despite these slight differences, the C₆₀ and C₆₀ and C₆₀H _{x} spectra are extremely similar in this range, which is somewhat surprising bearing in mind the differences between the molecular structures and the types of crystal lattices [simple cubic for C₆₀ (77 K) and body-centred cubic for C₆₀H _{x} ($x \approx 23$)].¹¹⁰

3. The structure and isomers of fullerene hydrides

The hydride C₆₀H₃₆ was first obtained by an extremely nontraditional method, namely by the Birch reduction of the C=C double bonds. It was therefore postulated that the hydride C₆₀H₃₆ contains 12 isolated double bonds in the molecule, one in each five-membered ring.²⁹ However, subsequently the compounds C₆₀H₃₆ were obtained also under other conditions.^{45,56,61,80–84} Furthermore, the structure with isolated double bonds for the fullerene hydride C₆₀H₃₆ does not explain the inhibition of the reduction after the addition of 36 hydrogen atoms to C₆₀.

The most symmetrical C₆₀H₃₆ isomer has 12 double bonds, which are disposed in each five-membered ring and belongs to the T_h symmetry group.^{29,116} The introduction of double bonds into the six-membered rings leads to a structure with a lower point group symmetry T in which there are four benzenoid fragments on the surface of the C₆₀H₃₆ molecule located at the corners of the tetrahedron.^{102–104} The less symmetrical structures with the D_{3d} and S_6 symmetries,^{61,116} in each of which there are two six-membered rings comprising hydrogen-free carbon atoms located at the poles of the molecule along the threefold axis, are intermediate between these extreme structures. The remaining six double bonds are isolated and disposed along the meridians and parallels of the D_{3d} and S_6 spheres respectively (Fig. 5).

The structures and stabilities of 63 C₆₀H₃₆ isomers have been analysed (the total number of C₆₀H₃₆ isomers is 6.1×10^{14} , but after the introduction of a series of restrictions, including threefold axes, their number diminishes to 63); one of them has the tetragonal T symmetry, four have the D_{3d} symmetry, three have the S_6 symmetry, nine have the C_{3v} symmetry, and four isomers have the C_3 symmetry.¹¹⁷ Detailed theoretical analysis of the C₆₀H₃₆ structures confirmed that the isomers with the D_{3d} and T molecular symmetries were the most stable.

The relative energies, the electronic structures, and the geometries of four isomers of the C₆₀H₃₆ molecule have been calculated by the semi-empirical local density functional (LDF) method (Fig. 5): the symmetries are T , T_h , S_6 , and D_{3d} .¹⁰⁵ It was found that the isomer with the T symmetry is energetically the

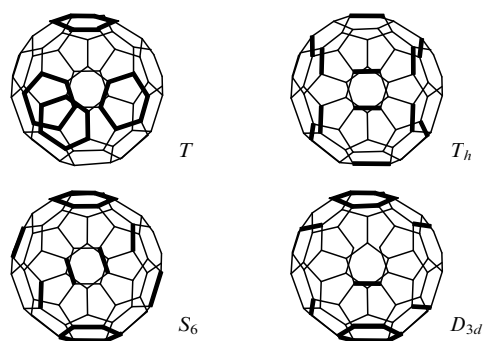


Figure 5. The structural isomers of $C_{60}H_{36}$.¹⁰⁵

most stable, which agrees with the semi-empirical AM1 calculations,¹⁰⁴ according to which this isomer is more stable than the isomer with the T_h symmetry by 0.7 eV. It may be that the stability of the isomer with the T symmetry, associated with the presence of aromatic rings, is the cause of the inhibition of the more extensive reduction of fullerene.⁵⁸ The smallest disruption of the initial fullerene skeleton and the greatest gain of the electron delocalisation energy are characteristic of the structure of the $C_{60}H_{36}$ molecule with the T symmetry. Furthermore, this structure agrees best with the available experimental data.¹⁰³ The remaining unsaturated bonds in the isomer with the T symmetry are of the 6–6 type. The ionisation potentials of all the $C_{60}H_{36}$ isomers lie within the range 6.47 ± 0.05 eV and the electron affinity is -0.24 ± 0.03 eV (Table 3).

Theoretical calculations have shown^{102–106} that the conjugated structure should be the most stable. It is significant that some of the eight $C_{60}H_4$ isomers, which exist and have been isolated,^{38,42} may be built up to the $C_{60}H_{36}$ T isomer on further reduction without any rearrangement of those double bonds of the molecule which are not involved in the reaction. The hydride $C_{60}H_{36}$ may be obtained also by the reduction of the octahedral $C_{60}H_{12}$, which is present among the hydrogenation products.

Since, like $C_{60}H_{36}$, the hydride $C_{70}H_{36}$ is distinguished by a high resistance to further reduction, there may apparently exist common causes which would explain this feature. In particular, steric causes (the mutual repulsion of the hydrogen atoms) should not be decisive in view of the fact that, since 36 hydrogen atoms ensure the maximum stability of the exohedral hydride of the C_{60} fullerene, in the case of C_{70} the maximum number of hydrogen atoms which may be added to the hydrocarbon skeleton without a significant increase in the overall energy should be greater.

In order to account for the characteristic features of the $C_{70}H_{36}$ molecule, structures A–C have been subjected to a theoretical analysis (Fig. 6).⁵⁸

(1) Structures A and C have the C_s symmetry, while structure B has the C_2 symmetry. The last structure is most uniformly hydro-

Table 3. Energy characteristics of the $C_{60}H_{36}$ isomers.¹⁰⁵

Symmetry	Relative energy/eV	Ionisation potential/eV	Electron affinity/eV	HOMO	LUMO
T_h	2.10	6.49	−0.27	$27t_u$	$7a_u$
T	0.00	6.52	−0.21	$17e$	$50t$
D_{3d}	2.35	6.48	−0.23	$33e_u$	$34e_g$
S_6	0.43	6.40	−0.23	$33e_u$	$34e_u$

genated and has 18 hydrogen atoms in each hemisphere of the molecule. (2) The calculated resonance energies suggest that the hydride $C_{70}H_{36}$ exists as a mixture of three isomers and that the compound with structure B should predominate, in conformity with its high symmetry. (3) Just as addition to the 9,10-bond in phenanthrene leads to a small change in resonance energy, addition to the analogous bonds of the phenanthrene-like formations in structures A–C leads to a slight loss of conjugation (80 kJ mol^{−1} for each C^{16} – C^{17} and C^{28} – C^{29} double bond in A and C^{16} – C^{17} and C^{61} – C^{62} in B; there is a similar loss of 94 kJ mol^{−1} for the C^{65} – C^{66} bond in isomer C). The model predicts the formation of $C_{70}H_{38}$ and to a lesser extent of $C_{70}H_{40}$ on further hydrogenation, which has been confirmed experimentally.^{56,80,84} (4) Structures A–C may be obtained by reducing the $C_{70}H_4$ isomers, which really exist.^{38,42}

Further reduction of the stable $C_{60}H_{36}$ and $C_{70}H_{36}$ becomes possible only by overcoming the high energy barrier, which presumably corresponds to the hydrogenation of the six-membered fragments.⁵⁸ In this case, the reduction of $C_{60}H_{36}$ should proceed via stepwise hydrogenation with formation of the hydrides $C_{60}H_{36} + n$ ($n = 6, 12, 18, 24$) and there is experimental evidence for the existence of the compounds $C_{60}H_{42}$ and $C_{60}H_{48}$.^{47,83} The reduction of structures A and B for the composition $C_{70}H_{36}$ should take place via multistage hydrogenation with formation of the hydrides $C_{70}H_{36} + n$, namely $C_{70}H_{46} \rightarrow C_{70}H_{52} \rightarrow C_{70}H_{58} \rightarrow C_{70}H_{64} \rightarrow C_{70}H_{70}$, whereas the reduction of structure C should proceed as $C_{70}H_{42} \rightarrow C_{70}H_{46} \rightarrow C_{70}H_{52} \rightarrow C_{70}H_{58} \rightarrow C_{70}H_{64} \rightarrow C_{70}H_{70}$. Since there is a greater loss of resonance energy on formation of $C_{70}H_{70}$ from $C_{70}H_{36}$ (~ 1060 or ~ 31 kJ mol^{−1} for each C=C bond) than on formation of $C_{60}H_{60}$ from $C_{60}H_{36}$ (~ 602 or ~ 25 kJ mol^{−1} respectively), the synthesis of perhydrofullerene $C_{70}H_{70}$ appears even more difficult.⁵⁸

It follows from the foregoing that in principle there may exist three stable $C_{70}H_{36}$ isomers, namely two isomers with two phenanthrene-like and one benzenoid rings and one isomer with one phenanthrene-like and one naphthenoid rings. The increased stability of such structures, associated with the presence of aromatic fragments, prevents their further reduction.

Another study¹⁰⁶ has also been devoted to the question of the stability of various structures of the fullerene hydrides $C_{60}H_{36}$ and $C_{70}H_{36}$. The results of the calculations showed that the formation

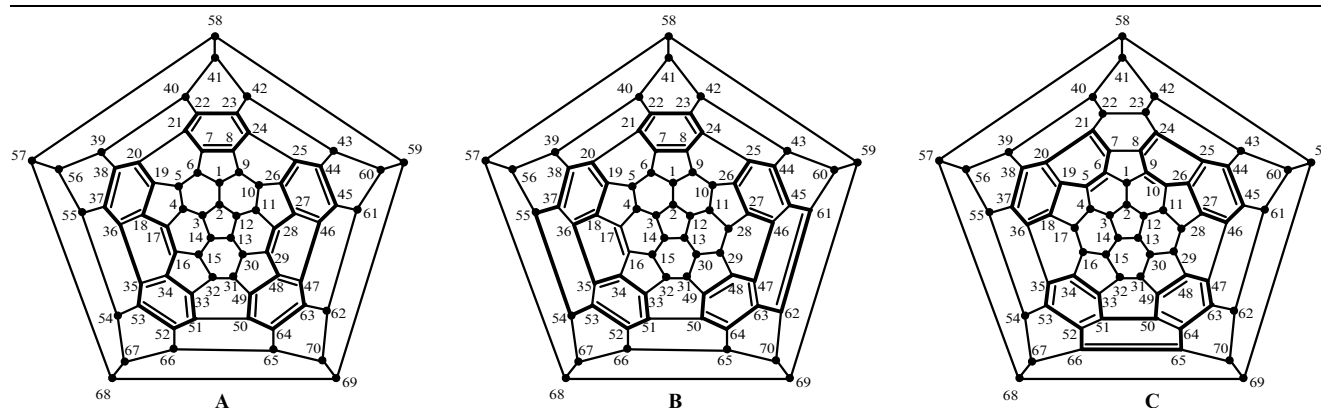


Figure 6. The structural isomers of $C_{70}H_{36}$.⁵⁸

energy of the $C_{60}H_{36}$ isomers with the T symmetry is lower by $97.4 \text{ kcal mol}^{-1}$ than the formation energy of the T_h isomer, which confirms the general conclusion reached in other investigations (for example that of Taylor¹⁰²) that the real $C_{60}H_{36}$ structure has the T symmetry. For $C_{70}H_{36}$, structures in which the hydrogen atoms are located at the poles of the molecule in the 1,2,3-positions in the 12 five-membered rings have been considered. Since in this case a graphite-like region with a high degree of conjugation is formed in the equatorial region of the fullerene skeleton, the isomers corresponding to this model should have low formation energies.

The structure of $C_{70}H_{36}$ has also been calculated by methods of molecular mechanics⁴⁷ on the assumption that after reduction the reaction product contains only nonconjugated double bonds or double bonds resembling aromatic bonds which are unreactive in relation to hydrogen transfer.⁴⁴ In each of the 12 five-membered rings of the carbon cluster, there is one double bond; there is one double bond also at each pole of the $C_{70}H_{36}$ molecule, whilst the remaining ten cyclopentene rings are joined together in such a way that a pentaphenylene strip is formed in the equatorial region. The enthalpy of formation of the hydride $C_{70}H_{36}$ (corresponding to the proposed model) has been calculated as $\Delta H_f^\circ(g) = 490.2 \text{ kcal mol}^{-1}$. Further reduction of $C_{70}H_{36}$ with formation of $C_{70}H_{40}$ leads to an increase in $\Delta H_f^\circ(g)$ to $535.7 \text{ kcal mol}^{-1}$.

4. Electronic and IR spectra of fullerene hydrides

The lower fullerene hydrides, for example $C_{60}H_2$, retain the C_{60} structure, which is reflected in their UV and visible spectra.³³ A characteristic feature of the formation of the 1,2-addition product is the appearance in the electronic spectrum of bands at ~ 430 and $\sim 700 \text{ nm}$ ³⁹ (436 and 702 nm for $C_{60}H_2$). The formation of $C_{60}H_4$ (the addition of H_2 to the second double bond) is accompanied by the disappearance of the band at 700 nm. The absorption at 220 (230) nm is characteristic of $C_{60}H_{36}$.^{29,45} The most detailed spectra of $C_{60}H_{36}$ and $C_{70}H_{36}$, obtained by the reduction of the corresponding fullerenes in a saturated solution in hexane (inert atmosphere) in the Zn/conc. HCl system, have been published by Darwish *et al.*⁵⁶ (Fig. 3).

The absorption in the range 255–280 nm has been regarded as evidence for the presence of aromatic fragments of the benzene type in $C_{60}H_{36}$ and of phenanthrene-like fragments in $C_{70}H_{36}$.⁵⁸ The presence of these fragments in the fullerene hydride molecule has been demonstrated by the appearance of a charge-transfer band in the spectra of compounds of the type $C_{60}H_{36} \cdot TCNE$ ($TCNE = \text{tetracyanoethene}$).¹⁰⁷

The IR spectra of the hydrogenated derivatives of fullerenes agree with the presence of C–H and C=C bonds. Thus bands in the region of C–H stretching vibrations are present in the IR spectra of fullerene hydrides (Table 1) — they are weak in the case of the lower hydrides and intense for $C_{60}H_{36}$ and $C_{70}H_{36}$, the number of bands in the case of $C_{60}H_{36}$ depending on the method of synthesis of the hydride. For example, the IR spectrum of the hydride $C_{60}H_{36}$ obtained by radical hydrogenation consists of three intense C–H stretching vibration bands and a weak band at 1490 cm^{-1} band (together with other weaker bands).⁶¹ The bands at 1490, 1511, and 1606 cm^{-1} for $C_{60}H_{36}$ obtained by the transfer hydrogenation⁴⁵ lie in the region of the stretching vibrations of the C=C bonds.⁶¹ It has been noted that the intensity of the C=C bond vibration in the region of 1650 cm^{-1} diminishes on reduction under more severe conditions.⁸³

For the $C_{60}H_{36}$ molecule with the T_h symmetry, only one active C–H vibration should be observed in the IR spectrum, while for the molecules with the D_{3d} and C_{3i} symmetries one may expect at least 5 and 17 vibrations respectively. ¹³C NMR data as well as comparison of the experimental and calculated IR spectra for $C_{60}H_{36}$ enabled Attalla *et al.*⁶¹ to reach the preliminary conclusion that the $C_{60}H_{36}$ hydride which they obtained corresponds to the D_{3d} and not the T_h symmetry. At the same time, for a more exact assignment of the IR and NMR bands, the studies should probably be performed on individual specimens of the

hydrides of C_{60} and C_{70} fullerenes synthesised by the radical hydrogenation method.

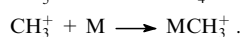
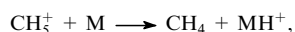
The IR spectrum of the fullerene hydride $C_{60}H_{36}$ obtained by Birch reduction contains bands characteristic of both aliphatic C–H and aromatic C=C bonds.¹⁰⁷ Comparison of the experimental IR spectra with the spectra calculated for the T and T_h structures showed that they are in better agreement with the structure having the T symmetry.¹⁰⁷

Bands due to the stretching vibrations of the hydrocarbon skeleton in the polyhydride $C_{60}H_x$ containing ~ 23 H atoms have been identified at 242, 306(s), 453(s), 524, 783, and 912 cm^{-1} . Compared with the vibrations of pure C_{60} , these vibrations have appreciably lower frequencies and differ significantly in the distribution of intensities, which confirms the expected weakening of the C–C bonds and the decrease in molecular symmetry as a result of the hydrogenation of the double bonds. The deformation vibrations of the C–H bonds in the hydride $C_{60}H_{23}$ are characterised by an intense broad ($\Delta\nu_{1/2} = 280 \text{ cm}^{-1}$) absorption band at 1250 cm^{-1} with a shoulder in the region of 1090 cm^{-1} .¹¹⁰ A similar peak is characteristic of hydrogenated amorphous carbon,^{114,115} which indicates the similarity of the C–H bonds in the two structures.

5. Mass spectrometry in the study of fullerene hydrides

Mass-spectrometric analysis plays a decisive role in the identification of the products of the hydrogenation of fullerenes. The MS analytical methods, differing in the method of vaporisation of the sample and the procedure used for its ionisation, may influence the result, therefore it is necessary to treat mass-spectrometric data with caution. The influence of differences in the analytical method on the results of the analysis has been most fully elucidated in the identification of the products of the Birch reduction of C_{60} .^{29,30} The composition of $C_{60}H_{36}$ was first determined from EI-MS data.²⁹ When the molecules are ionised by fairly soft electron impact in the gas phase, radical-cations are produced with a low internal energy — 2–8 eV (200–775 kJ), which is insufficient for the effective fragmentation of the excited species. This ionisation method is therefore fully suitable for the solution of a series of problems associated with the determination of the molecular structure of the hydride. However, the EI-MS method suffers from a number of disadvantages: in combination with the most readily available method involving vaporisation from a Knudsen cell, it is applicable only to the analysis of thermally stable volatile organic compounds; furthermore, in certain cases the fragmentation of ions with an odd number of electrons, formed on electron impact, proceeds so effectively that the mass spectra contain no molecular ions. The use of the EI-MS and LD-MS methods for the study of $C_{60}H_{36}$ obtained by the radical hydrogenation method proved impossible owing to the thermal decomposition of $C_{60}H_{36}$ to lower-molecular-mass compounds: $C_{60}H_{18}$, $C_{60}H_8$, *etc.*⁶¹ The elimination of hydrogen from the unstable fullerene hydrides ($C_{60}H_n$, $n > 36$) on laser desorption has also been noted by Gerst *et al.*⁴⁷

One of the most important 'mild' and selective ionisation methods is chemical ionisation (CI), which is usually achieved as a result of ion–molecule reactions between neutral molecules of the substances analysed and the ions derived from the reagent gas (methane, isobutane, and ammonia are the most frequently used). The reagent gas ions are as a rule obtained by bombardment with electrons having energies of 100–500 eV at a pressure of 10^{-10} – 10^{-2} Pa in the ion source. The collisions of the ions formed with the molecules of the reagent gas result in the formation of reagent ions with an even number of electrons (CH_3^+ and CH_5^+ from methane), which then react with the molecules of the substances analysed. They protonate the molecules of these substances or form adduct ions with them, for example:



The ions with an even number of electrons generated on chemical ionisation are more stable than the ions with an odd

number of electrons formed on electron impact, so that the mass spectra of the ions generated as a result of chemical ionisation contain the intense peaks due to the adduct ions (or cluster ions) or protonated ions, while the peaks of the fragment ions have low intensities or are absent altogether.

Ionisation methods such as field desorption, secondary ion mass spectrometry, bombardment by fast atoms, laser desorption, *etc.* are also used for the analysis of involatile and thermally unstable compounds.¹¹⁸ When FD-MS is used, there is no need to vaporise the sample. The sample of solution or suspension is deposited on an activated emitter and the temperature of the latter is chosen to ensure sufficient intensity of the molecular ion peak in the spectrum accompanied by minimal fragmentation (usually 300–600 K). Indirect heating of the emitter with the aid of a laser has sometimes proved more effective as regards the formation of molecular ions.

Fullerene hydrides have been studied⁴⁵ mass spectrometrically with the aid of various methods, including electron impact, bombardment by fast atoms, and field desorption. M^+ and sometimes M^{2+} peaks are usually present in the $C_{60}H_{36}$, $C_{60}D_{36}$, $C_{60}H_{18}$, and $C_{60}D_{18}$. It has been noted that in the analysis of the above hydrides by the electron impact method, partial fragmentation, accompanied by loss of hydrogen and the appearance of free C_{60} , is observed. The field desorption method gives rise to only the M^+ peak. The FAB method yielded satisfactory results in the analysis of the fullerene dihydride prepared by the reduction of C_{60} with diborane, but its application to other hydride specimens proved difficult (see, for example, Avent *et al.*³⁸ and Becker *et al.*⁸⁷).

It has been found with the aid of 'mild', mutually complementing mass-spectrometric methods, such as time-of-flight mass spectrometry with vaporisation of the test substance by laser desorption and subsequent laser photoionisation, ion-cyclotron mass-spectrometry with laser desorption, and secondary ion-spectrometry, that a mixture of polyhydrofullerenes with compositions ranging from $C_{60}H_{18}$ to $C_{60}H_{36}$ is indeed formed in the course of the Birch reduction of C_{60} , the main product being $C_{60}H_{32}$.³⁰ When the L^2 TOF-MS method was used to analyse fullerene hydrides in the mass range 740–760 a.m.u., the resolution of the instrument proved insufficient for the determination of the mass distribution of the hydrides. Nevertheless, the mass spectrum obtained with the aid of L^2 TOF-MS yields no evidence for the formation of $C_{60}H_{36}$ as the main product. The ICR-MS method made it possible to obtain a spectrum with a well resolved series of peaks grouped around the main peak with a mass number of 753 ($752 + H^+$), corresponding to the distribution of the reaction products. The appearance of weak peaks in the range m/z 720–730 has been attributed to the fragmentation of the products to low-molecular-mass hydrofullerenes. Finally, the mixture was characterised with the aid of the SIMS method, which yielded a very well resolved spectrum, from which the exact distribution of the hydrogenation products was obtained (Fig. 7).³⁰

Thus the difference between the compositions of fullerene hydrides^{29,30} is frequently associated with the difference between

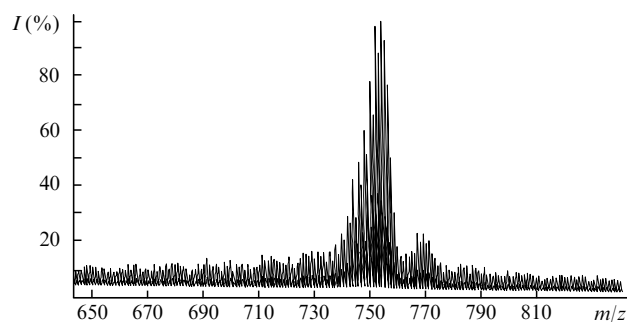


Figure 7. Mass spectrum of the products of the Birch reduction of C_{60} obtained by means of SIMS (matrix — 3-nitrobenzyl alcohol).³⁰

the methods used for mass-spectrometric analysis and can be accounted for by the thermal lability of the mixture of hydrogenated fullerenes on prolonged exposure to the high ($> 250^\circ C$) temperature necessary for the mass-spectrometric study by the method involving the direct introduction of the heated sample.

6. ^1H and ^{13}C NMR spectroscopy

The ^1H NMR spectrum of the hydride $1,2-C_{60}H_2$ contains a singlet at $\delta = 5.93$ ppm (toluene- d_8), which does not change in the range from -80 to $100^\circ C$. On the other hand, there are no well resolved and stable, in terms of time, ^1H NMR spectra of either $C_{60}H_{36}$ or $C_{70}H_{36}$. The broad bands with δ in the region from 2.5 to 4.2 ppm and a maximum at 3.80 ppm (for comparison, we may note that δ for dodecahedrane protons is 3.38 ppm), which refer to $C_{60}H_{36}$,^{29,45} agree poorly with the symmetrical structure for which the ^1H NMR spectrum should consist of narrow lines.⁵⁶ The spectra presented refer as a rule to either mixtures of hydrofullerenes or, if one is dealing with an individual compound, to a mixture of isomers. Finally, the broadening of the bands may be a result of the oxidation of fullerene hydrides by atmospheric oxygen in the presence of light. The attempts to obtain NMR spectra in more concentrated solutions, for example in CS_2 (the $CS_2-C_6D_6$ solvent mixture has been used in the case of lower fullerene hydrides of the type $C_{60}H_4$ ³⁸) proved unsuccessful owing to the interaction of CS_2 with $C_{60}H_{36}$ ⁵⁶ observed for the first time in this way. The observation of satisfactory spectra at a low concentration of the test substance requires a long time, which leads to the decomposition of the specimen in the presence of oxygen.

Even in the case of individual C_{60} hydrides, the physicochemical properties of specimens of the same composition but prepared by different methods are different, which may be associated with structural differences.

A complex multiplet with $\delta = 2.1-4.25$ ppm is manifested in the ^1H NMR spectrum of the catalytic hydrogenation products.⁸³ A spectrum with $\delta = 2.5-4.5$ ppm has been published for $C_{60}H_{36}$ obtained by the Birch method.²⁹ The appearance of additional signals in the range 2.1–2.5 ppm may be associated with the products of the more far reaching hydrogenation of fullerene.⁸³

At least four types of sp^3 -hybridised carbon atoms with $\delta = 31, 38, 44$, and 49 ppm and three types of sp^2 -hybridised carbon atoms with $\delta = 128, 134$, and 138 ppm are manifested in the solid-state ^{13}C NMR spectra of a reduced mixture of C_{60} and C_{70} .⁶¹ Integration yields the ratio $sp^2:sp^3 \approx 22:38$. When account is taken of the integration error, this ratio corresponds satisfactorily to the presence of a hydride with 36 hydrogen atoms. Analysis of the ^{13}C NMR spectrum led the authors⁶¹ to the conclusion that a structure with the D_{3d} symmetry may be assigned to the compound $C_{60}H_{36}$.

The structure of the hydride $C_{60}H_{36}$ formed on Birch reduction of C_{60} has also been investigated by Govindaraj.¹⁰⁷ The results agree with the data of Haufler *et al.*²⁹ but their interpretation is different. Thus the ^{13}C NMR spectrum of the hydride $C_{60}H_{36}$ obtained by the Birch method contains signals with $\delta = 140$ and 40 ppm, which Govindaraj¹⁰⁷ assigns to aromatic and saturated carbon atoms respectively. The signals of the carbon atoms in the aromatic ring proved weaker than might have been expected (apparently owing to the quaternary nature of these atoms). According to Govindaraj,¹⁰⁷ these spectra confirm a structure with the T symmetry for $C_{60}H_{36}$. The UV spectrum of this compound contains bands at 218 and 275 nm. Govindaraj¹⁰⁷ believes that the band at 275 nm indicates the presence of an isolated aromatic fragment in the $C_{60}H_{36}$ molecule (see also Darwish *et al.*⁵⁶). The presence of such an isolated benzene ring is demonstrated by the appearance of a charge-transfer band (305 nm) when $C_{60}H_{36}$ interacts with tetracyanoethene¹⁰⁷ (in the benzene-TCNE system, the charge-transfer band is at ~ 300 nm¹¹⁹). It has been suggested that the hydride $C_{60}H_{36}$ with the T symmetry and having isolated double bonds is formed initially during the hydrogenation reaction and is then transformed via sigmatropic shifts into a thermodynamically more stable molecule

with the T symmetry and isolated benzene rings. This hypothesis has been confirmed by the synthesis by the method of Rüchardt *et al.*⁴⁵ of a $C_{60}H_{36}$ specimen stable in the solid state.

The ^3He chemical shifts in the ^3He NMR spectra of the possible isomers of the endohedral complexes $\text{He}@C_{60}H_{36}$ have been calculated.⁶² The calculated shifts for different isomers (the type of symmetry is indicated in brackets) of $\text{He}@C_{60}H_{36}$ are $-10.8(T)$, $-7.4(D'_{3d})$, $-6.1(S_6)$, $-3.4(T_h)$, and -5.6 ppm (D_{3d}).⁶² The calculation also confirmed that the chiral structure with the T symmetry is the most stable among the possible $C_{60}H_{36}$ isomers (the T structure is more stable than the T_h structure by 59 kcal mol^{-1}). The authors⁶² suggest that the experimental investigation of compounds of the type $\text{He}@C_{60}H_{36}$ will yield new information about the composition of the C_{60} hydrogenation products.

7. Photophysical properties of fullerene hydrides

The photophysical properties of three hydrofullerenes have been investigated at room temperature in solution in toluene: $C_{60}H_2$, $C_{60}H_4$, and 2,3-[1-(3-carboxypropionyloxymethyl)-4-methylbut-2-enol]buckminsterfullerene **2** (the last compound has a hydrophilic substituent linked to the hydrophobic C_{60} skeleton).¹²⁰ The visible absorption spectra of these compounds in the ground state were compared with the spectra of methanofullerenes and methanofulleroids.[†] The changes observed in the spectra of methano- and hydro- fullerenes compared with the spectra of C_{60} and methanofulleroids are associated with the differences between the electronic structures of these molecules (58 and 60 π -type electrons respectively). The absorption spectra of $C_{60}H_2$, $C_{60}H_4$, and compound **2** in the triplet state are similar ($\lambda_{\text{max}} \approx 700 \text{ nm}$ for $C_{60}H_2$ and compound **2** and $\lambda_{\text{max}} \approx 710 \text{ nm}$ for $C_{60}H_4$). The quantum yield in the formation of the photosensitised $^1\text{O}_2(^1\Delta_g)$ in the presence of $C_{60}H_2$, $C_{60}H_4$, and compound **2** is close to unity, as in the case of C_{60} . The high effectiveness of the generation of singlet oxygen is probably the cause of the frequently observed degradative changes in the structures of fullerene hydrides in solution.^{33,45,56} The molar absorption coefficients of $C_{60}H_2$, $C_{60}H_4$, and compound **2** in the excited triplet state have been calculated as $\sim 10\,500$ (at 700 nm), ~ 4800 (at 710 nm) and $\sim 11\,000 \text{ mol litre}^{-1} \text{ cm}^{-1}$ (at 700 nm) respectively.

8. The acidity and strength of the C–H bonds in fullerene hydrides

The voltammetric method has been used to investigate the acid–base reactions of hydrogenated fullerenes in solution in dimethyl sulfoxide (DMSO).¹²¹ According to Guarr *et al.*¹²² and Boulas *et al.*,¹²³ dihydrofullerene $C_{60}H_2$ gives rise to three reversible reduction peaks (the radical-anion, dianion, and trianion) with potentials approximately 0.1 V more negative than the corresponding potentials of C_{60} in the 67:33 (by volume) DMSO–toluene mixture. It was noted that $C_{60}H_2$ decomposes slowly in this medium to C_{60} . A series of bases were used to deprotonate $C_{60}H_2$ and to determine the acidity.



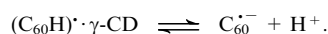
$$K_1 = \frac{[C_{60}H^-][BH]}{[C_{60}H_2][B^-]}.$$

(B^- represents the sodium salts of dichloroacetic acid, saccharin, and trifluoroacetic acid; the pK_a for these acids in DMSO are 6.4, 4.0, and 3.45 respectively).

The values of pK_a (1) and pK_a (2) (for the first and second dissociation constants) found for $C_{60}H_2$ are 4.7 and 16 respectively (DMSO, 298 K). The acid dissociation constant of the C–H bond in $\text{Bu}^tC_{60}H$ is 5.7.¹²⁴ The replacement of the *tert*-butyl group

by hydrogen leads to an increase in acidity by virtue of the stronger electron-donating character of the *tert*-butyl group compared with hydrogen.

By employing the sensitivity of the absorption band of the complex of the $C_{60}^{\bullet-}$ radical-anion and γ -cyclodextrin (γ -CD) at 1080 nm in the near IR, the pK_a of the conjugate acid ($C_{60}H$)[•] was determined in the 9:1 H_2O – Pr^iOH mixture and was found to be $4.5 (\pm 0.5)$.¹²⁵



A pK_a of the same order of magnitude has been quoted for $\text{HC}_{60}^{\bullet}$ in dichlorobenzene.¹²⁶ On the other hand, in DMSO the value $pK_a = 9$, was obtained for $\text{HC}_{60}^{\bullet}$ by Niyazymbetov *et al.*¹²¹ The high acidity of $\text{HC}_{60}^{\bullet}$ is combined with a low strength of the C–H bond (71 kcal mol^{-1} for $\text{Bu}^tC_{60}H$).¹²⁴ We may note that quantum-chemical calculations yield C–H bond energies in $C_{60}H_{12}$ (73 kcal mol^{-1}) and $C_{60}H_{18}$ – $C_{60}H_{36}$ (70 – 71 kcal mol^{-1})¹⁰⁴ which are close to the experimental C–H bond strengths in fullerene monohydride.¹²⁴ The calculated average C–H bond energy in $C_{60}H_{60}$ is $\sim 62 \text{ kcal mol}^{-1}$. Such a decrease is caused by the significant structural strain in the fully saturated hydrocarbon framework.¹⁰⁴

Electrolysis of C_{60} to give C_{60}^{2-} with subsequent protonation constitutes an alternative free-radical method of synthesis of $C_{60}H_2$.¹²⁶ The stepwise protonation of the dianion showed that the first proton adds more readily than the second.

An attempt has been made to create a pK_a scale for the hydrofullerene series.¹²⁷ The calculated acidities confirm the hypothesis² that the acidity of fullerene hydrides diminishes with increase in the degree of hydrogenation. In this sense, fullerene monohydride $C_{60}H$ should have the most acidic aliphatic C–H bond.

9. X-ray photoelectron spectroscopy in the study of fullerene hydrides

The fullerene hydride $C_{60}H_{36}$ synthesised by reducing C_{60} with dihydroanthracene in the melt⁴⁵ has been investigated by electron energy loss spectroscopy (EELS).¹²⁸ Fig. 8 presents the loss functions for $C_{60}H_{36}$ and C_{60} . Both functions have a similar form, but the maximum due to the oscillations of all the valence electrons [the $(\sigma + \pi)$ -plasmon] is located at a lower position as regards energy in the case of the hydride (23.8 eV) than in the case of solid C_{60} (25.0 eV). This means that the valence electron density, determined by the magnitude of this energy, diminishes on passing from C_{60} to $C_{60}H_{36}$. The relative intensity of the peak associated with the excitation of the π -plasmon also decreases appreciably in this transition. Under these conditions, the π -plasmon peak loss energy hardly changes. With increase in the irradiation time, the form of the loss function for $C_{60}H_{36}$ becomes similar to that of the function for C_{60} , which is apparently associated with the evolution of hydrogen from the hydride.

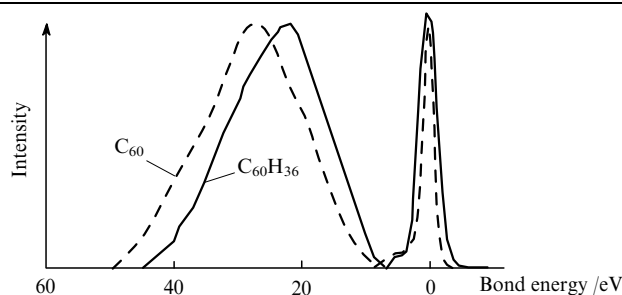


Figure 8. The loss functions for the hydride $C_{60}H_{36}$ (continuous line) and fullerene (dashed line) in the EELS spectra.¹²⁸

10. Electrochemistry of fullerene hydrides

In many respects, the electrochemical behaviour of $C_{60}H_2$ is similar to the behaviour of C_{60} fullerene, but $C_{60}H_2$ is reduced

[†] Methanofullerenes and methanofulleroids differ in the way that the ligand is attached to the double bonds of fullerene: addition to the 6–6 bonds with retention of the fullerene framework and the formation of a cyclopropane ring in the former case and the opening of the 6–5 bond in the case of methanofulleroids.

with somewhat greater difficulty.¹²² The potentials $E_{1/2}$ for the reduction of $C_{60}H_2$ in various solvents are presented in Table 4.¹²²

Table 4. Electrochemical reduction of $C_{60}H_2$.¹²²

Solvent ^a	$E_{1/2} (C_{60}H_2^{2-}/C_{60}H_2^{(z+1)-}) / V$ rel. to Fc^+/Fc			
	0/1—	1—/2—	2—/3—	3—/4—
PhMe—CH ₃ CN	−1.05	−1.44	−1.99	−2.36
PhCN	−1.04	−1.43	−2.01	
CH ₂ Cl ₂	−1.11	−1.48	−1.99	

^a 0.1 M (C₄H₉)₄NPF₆ was used as the electrolyte.

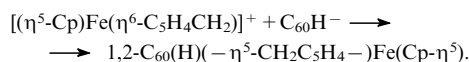
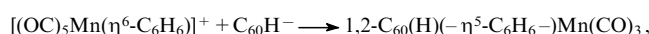
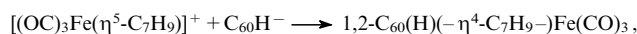
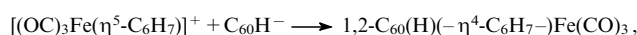
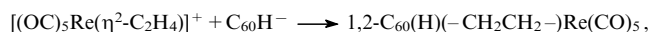
The electrochemical properties of $C_{60}H_2$ and 1.9- and 7.8- $C_{70}H_2$ in the DMF–toluene mixture have been investigated.¹²³ $E_{1/2} = -1.02, -1.46, -2.07$, and -2.58 V (relative to Fc/Fc^+) have been obtained for $C_{60}H_2$. Owing to the lower solubility of the reduced $C_{70}H_2$ isomers in the DMF–toluene mixture, it is possible to observe only three consecutive electron transfers for these substances. Thus $E_{1/2} = -1.04, -1.48$, and -1.96 V (relative to Fc/Fc^+) have been obtained for 7.8- $C_{70}H_2$, while the corresponding values for 1.9- $C_{70}H_2$ are $-1.03, -1.52$, and -1.93 V. The electronic effects in these isomers, having different stabilities, are not reflected in their electrochemical behaviour. The stability of the reduced hydride derivatives decreases with increase in the charge, temperature, and (or) the content of DMF in the DMF–toluene mixture. The singly charged radical-anion $C_{60}H_2^-$ proved to be the most stable among the reduced compounds (the EPR spectrum of $C_{60}H_2^-$ is characterised by $g = 2.000$ and $\Delta H = 3$ G at 160 K, whereas the EPR spectrum of C_{60}^- has $g = 1.997$ and $\Delta H = 5.8$ G).¹²³

The electrochemical oxidation of $C_{60}H_2$ has been investigated in PhCN. It is irreversible and takes place in two stages. In the first stage, C_{60} is formed from $C_{60}H_2$ as a result of the loss of two protons and two electrons, and then oxidised in the second stage at more positive potential ($E_p = 1.13$ and 1.35 V relative to Fc/Fc^+).

11. Reactions of fullerene hydrides

The anion $C_{60}H^-$ exhibits fairly strong nucleophilic properties. It is formed when stoichiometric amounts of C_{60} and $LiEt_3H$ are mixed in toluene.¹²⁹ Methyl iodide does not alkylate this compound,¹²⁹ whereas $Et_3O^+BF_4^-$ in dichloromethane reacts with $C_{60}H^-$ to form 1,2- $C_{60}(H)(Et)$ in a quantitative yield. The ¹H NMR spectrum of the product of the reaction of $C_{60}H^-$ with $Et_3O^+BF_4^-$ in CS_2-CDCl_3 [$\delta = 6.42$ (s, 1 H, $C_{60}H$), 3.50 (q, 2 H, CH_2), 2.09 (t, 3 H, CH_3)]¹³⁰ agrees with that described by Hirsch *et al.*¹³¹ The anion $C_{60}H^-$ is protonated by HBf_4 in ether with formation of 1,2- $C_{60}H_2$, giving rise to a singlet at $\delta = 5.93$ in toluene- d_8 .¹³⁰

The addition of nucleophiles to unsaturated ligands in cationic metal complexes, well known in organometallic chemistry, proceeds smoothly also in the reaction with $C_{60}H^-$, the unsaturated ligands serving as a bridge between fullerene and the metal.¹³⁰



The ¹H NMR spectra of these complexes exhibit a signal in the range $\delta = 5.9-6.5$ ppm, characteristic of the compounds 1,2- $C_{60}(H)(R)$.^{3,132} The mass spectra of the products indicate that the molecular ions 1,2- $C_{60}(H)(RML_x)^{+*}$ decompose mainly via the β -elimination mechanism with formation of C_{60}^+ . The com-

pound 1,2- $C_{60}(H)[CH_2CH_2Re(CO)_5]$ decomposes as a result of double β -elimination to C_{60}^+ , $H_3CCH_2Re(CO)_5^+$ and $HRe(CO)_5^+$. Thus a convenient method has been proposed¹³⁰ for the synthesis of metal complexes in which fullerene is linked to the metal atom not directly but via a carbon bridge.

IV. Conclusion

The history of the study of fullerene hydrides covers only a few years, but, despite the preliminary nature of many investigations and the controversial character of certain conclusions, it is already clear that a long life in science and technology lies ahead of this field. The report concerning the study of the structure of the individual hydride $C_{60}H_{18}$ by the ¹H NMR method may be regarded as a consecutive advance in this direction.¹³³ The hydride $C_{60}H_{18}$, obtained by the solid-phase hydrogenation method, has the C_{3v} symmetry according to ¹H NMR data. The study by the differential scanning calorimetry (DSC) of the thermal stability of the highly pure $C_{60}H_{36}$ showed that, together with the dehydrogenation of $C_{60}H_{36}$ to C_{60} , processes involving the degradation of the carbon skeleton of the fullerene take place.¹³⁴

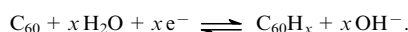
The great potential possibilities for the practical employment of systems based on fullerene hydrides have also promoted the rapid development of the relevant research. One may postulate the possibility of creating electrochemical cells employing intermetallic compounds — fullerene hydride compositions as cathodic materials, as well as the creation of reversible hydrogen accumulators.

The possibility of employing a wide temperature range and of the chemical modification of fullerenes makes it possible to regulate their reactivity in relation to hydrogen. This is of fundamental importance for the creation of active catalysts of the reactions of hydrocarbons. For example, the crystalline adducts of fullerenes with alkali metals, certain representatives of which (M_3C_{60}) exhibit superconducting properties, are capable of catalysing effectively even at -100 °C the homonuclear isotope exchange of hydrogen.¹³⁵ At 300 K and a pressure of the $H_2 + D_2$ mixture of 100 Torr, the reaction rate constant for the Cs_6C_{70} catalyst is 10 min^{-1} . It is 60 times greater than for the caesium compound of graphite having the same composition. The activation energy for the reaction is 11.1 kJ mol^{-1} . In the presence of the Cs_6C_{70} catalyst, ethene is hydrogenated by hydrogen already at 373 K and the rate constant at a pressure of the $C_2H_4 + H_2$ mixture of 200 Torr is 0.5 min^{-1} . The proposed process mechanism involves the dissociative adsorption of the H_2 molecule on the hydrocarbon framework with formation of fullerene hydrides (H_2 is activated similarly on the noble metals platinum and palladium).¹³⁵

The dehydrogenating activity of fullerene catalysts in relation to alkanes,⁵⁰ including methane,^{52,53} exhibited in the range of high temperatures, as well as the influence of hydrogen on the dehydrogenation process similar to that of catalysts based on noble metals,⁵³ makes it possible to regard fullerene catalysts as functional analogues of noble metals. The possibility of a wide variation of the composition of fullerene-containing catalysts and of the temperatures at which they are used makes fullerene structures promising catalysts for a wide variety of reactions of saturated hydrocarbons such as reforming, hydrocracking, dehydrogenation, and others of great industrial importance.

Catalysis with participation of fullerene hydrides may contribute to the recombination of hydrogen atoms with formation of H_2 occurring in interstellar space.¹³⁶ This fundamental hypothesis may be tested with the aid of laboratory studies of the absorption and emission spectra of fullerenes in the UV and IR ranges and by comparison with the spectroscopic characteristics of interstellar space. Another stage in testing the hypothesis may be the laboratory study of the possibility of achieving the bimolecular reaction involving the addition fullerene skeleton with radiation cooling of the excited adduct. Only the readily occurring termolecular addition of a hydrogen atom has now been demonstrated experimentally.¹³⁶

The problem of the reduction of fullerenes continues to interest investigators. The electrochemical hydrogenation of C_{60} in 30% aqueous KOH solution has been achieved.¹³⁷ The cathodic C_{60} reduction potential has been found to be -1.4 V (relative to Ag/AgCl). It has been shown that $C_{60}H_2$ is formed under these conditions, although the yield of the dihydride is low. The hydrogenation of C_{60} and the dehydrogenation of $C_{60}H_x$ during electrolysis are reversible.



Thus the possibility of using C_{60} as the electrode material for the creation of batteries in aqueous KOH has been demonstrated.

Preliminary results of the study of the reduction of higher (C_{76} , C_{78} , and C_{84}) fullerenes in the Zn–conc. HCl–toluene system in the dark and in the absence of oxygen have been reported.¹³⁸ The reduction of C_{76} leads to $C_{76}H_{46}$ – $C_{76}H_{56}$, while the reduction of C_{78} (according to the isomeric composition of the initial fullerene) affords a wide range of hydrogenation products, $C_{78}H_{48}$ being the main component. Products having the compositions $C_{84}H_{48}$ – $C_{84}H_{52}$ have been obtained as a result of the reduction of C_{84} . In each case, the reduction of higher fullerenes is accompanied by the degradation of the specimen and the appearance of the hydrides $C_{60}H_{36}$ and $C_{70}H_{36}$ and $C_{70}H_{40}$ (HPLC), which confirms yet again that the stability of these hydrides is a maximum and that the reduced C_{84} derivatives are least stable.

The photochemical reaction ($\lambda = 350$ nm, N_2 , 12 h) of C_{60} with tertiary amines $RNMe_2$ ($R = Ph, Me$) leads to products of the addition of the amine to the 6–6 bond of the fullerene.¹³⁹ On further irradiation of the reaction mixture in the presence of an excess of C_{60} , the adduct is converted into a pyrrolidine derivative of C_{60} and 1,2- $C_{60}H_2$, confirming thereby the possibility of reducing the fullerene when mixtures of fullerenes with organic compounds are irradiated.

The theoretical analysis of fullerene hydrides has been continued.^{140, 141} Structures with a skewed pentagonal-pyramidal disposition of hydrogen atoms have been considered. The addition of hydrogen to $C_{60}H_6$, $C_{60}H_{12}$, or $C_{60}H_{18}$ takes place mainly in the *ortho*-position, whereas the addition of bromine occurs preferentially in the *para*-position. Hydrogen and bromine are eliminated respectively from the *para*- and *ortho*-positions in one of the skewed pyramidal structures. The pentagonal-pyramidal $C_{60}H_6$, the doubly pentagonal-pyramidal $C_{60}H_{12}$, the triply pentagonal-pyramidal $C_{60}H_{18}$ and also $C_{60}H_{26}$, $C_{60}H_{28}$, and $C_{60}H_{36}$ do not disproportionate to higher and lower hydrides.

It has been shown with the aid of IR and ^1H NMR spectroscopy that, in the interaction of C_{60} with $HIr(C_8H_{12})(PPh_3)_2$ the transition metal atom is coordinated to the C_{60} molecule via the $C1$ – $C2$ bond.¹⁴²

It has been shown¹⁴³ that in the absence of oxygen in the dark and on irradiation, the interaction of C_{60} with $H_3Ir(PPh_3)_3$ leads to different products: to the complexes of iridium with η^2 -coordinated C_{60} on heating in toluene ($100^\circ C$) and to the oxidation of iridium by the triplet-excited C_{60} (Nd^{3+} : YAG laser, $\lambda = 532$ nm) on irradiation in benzonitrile. The photochemical reaction in benzonitrile leads to the appearance of an absorption band in the near IR and of an EPR signal for the C_{60} radical-anion ($\lambda = 1078$ nm, $g = 2.0001$). The triplet-excited C_{60} is quenched by the complex $H_3Ir(PPh_3)_3$ via a reductive mechanism, the quenching constant being $k_q = 1.1 \times 10^9$ mol $^{-1}$ s $^{-1}$.

It has been noted¹⁴⁴ that the appearance of a signal with m/z 780 (see, for example, Shigematsu *et al.*⁸³) in the mass spectrum of the C_{60} hydrogenation products when toluene is used as the solvent is probably associated with the formation of the trimethylene adduct of the fullerene hydride $C_{60}H_{18}$ and not with the formation of $C_{60}H_{60}$.

The optimum structures and the relative stabilities of the $C_{70}H_{36}$ molecule (the heats of formation of the isomers) have been calculated, which showed that the presence of aromatic fragments on the surface of the molecule is not the dominant factor determining the stability. The energy of the deformation of

the molecule owing to steric strain, induced by the fact that aromatic fragments must be planar, exceeds the resonance energy gained. A series of structures have already been proposed for $C_{70}H_{36}$ with partly isolated double bonds,¹⁴⁵ their calculated heat of formation being significantly lower than for the 'aromatic' isomers. The search for the optimum combination of aromaticity and steric strain in $C_{70}H_{36}$ isomers is being continued.¹⁴⁶

The photophysical properties of the hydrides $C_{60}H_{18}$ and $C_{60}H_{36}$, obtained with a purity of 90%–98% by the transfer hydrogenation⁴⁵ with subsequent purification by sublimation, differ significantly.¹⁴⁷ The absorption spectrum for the ground state of $C_{60}H_{36}$, measured in solution and in methylene chloride, indicates the presence of isolated benzenoid fragments in the structure of the hydride. They are present in the isomers with the T , S_6 , or D_{3d} point symmetry group and are absent from the most symmetrical T_h isomer. Furthermore, the energy calculated for the molecule with the T_h symmetry is higher by more than 2 eV than the energy of the most stable-isomer.¹⁰⁵ Additional information about the symmetry of $C_{60}H_{36}$ is provided by the group-theoretical study of the IR and Raman spectra of the specimens obtained and also by the solid-phase ^{13}C NMR spectrum, which contains signals due to several different sp^3 -hybridised carbon atoms instead of the single signal expected for the T_h structure.¹⁴⁷ Analysis of the entire set of data enabled the authors¹⁴⁷ to reject the T_h structure for $C_{60}H_{36}$ and to identify the structure with the S_6 symmetry as the most probable. This conclusion differs from the conclusion by the authors of earlier studies^{61, 112} that the $C_{60}H_{36}$ specimens obtained by direct hydrogenation at a high pressure have the D_{3d} symmetry. These were investigated by electron and X-ray diffraction and also with the aid of NMR and IR spectroscopy, the spectroscopic characteristics of the specimens differing significantly from those obtained by Bensasson *et al.*¹⁴⁷ These differences have been interpreted¹⁴⁷ as evidence that different synthetic methods afford $C_{60}H_{36}$ isomers having different symmetries.

However, within the limits of one method products with different isomeric compositions can apparently be formed. Thus the hydrogenation of C_{60} by 9,10-dihydroanthracene,¹⁴⁸ analogous to that described by Bensasson *et al.*¹⁴⁷ leads to a product containing as the main component the $C_{60}H_{36}$ isomer with the T symmetry. Its solid-state ^{13}C NMR spectrum contains three signals due to sp^3 -hybridised carbon atoms at 31.1, 37.2, and 44.1 ppm and three signals due to sp^2 -hybridised carbon atoms at 124.9, 134.7, and 137.3 ppm with an integral intensity ratio of 36:24.¹⁴⁸

The electronic absorption spectrum of $C_{60}H_{18}$ in the ground state differs greatly from the spectrum of $C_{60}H_{36}$ ¹⁴⁷ and its structure is very close to that of the spectrum of C_{60} , which suggests the presence in the $C_{60}H_{18}$ molecule of an analogous conjugation system of sp^2 -hybridised carbon atoms, but with the difference that they do not cover the entire surface of the sphere.¹⁴⁷ This agrees with the results of the analysis of the ^1H NMR spectra of $C_{60}H_{18}$ specimens obtained by the solid-phase hydrogenation method.¹³³ The absorption spectrum of the lowest $C_{60}H_{18}$ triplet, obtained by flash photolysis in benzene,¹⁴⁷ is also structurally very similar to the spectrum of the triplet–triplet absorption of C_{60} in benzene and is located in the identical wavelength range, which confirms the postulate that the type of conjugation present in the initial C_{60} is retained to a significant extent in $C_{60}H_{18}$. An additional argument in support of this claim is the similarity of the lifetimes of the lowest $C_{60}H_{18}$ triplet (210 μs)¹⁴⁷ and C_{60} (47 μs) in benzene. The quantum yield in the formation of the triplet $\phi_t(C_{60}H_{18}) < 0.12$, estimated from the results of the flash photolysis of solutions in benzene, is appreciably lower than $\phi_t \approx 1$ for C_{60} and the lowest hydrides $C_{60}H_2$ and $C_{60}H_4$.^{120, 147} This fact agrees with the very weak fluorescence of C_{60} , $C_{60}H_2$, and $C_{60}H_4$ (the quantum yield of the C_{60} fluorescence is $\approx 10^{-4}$) compared with the fairly intense fluorescence of $C_{60}H_{18}$.¹⁴⁷ Such modification of the photophysical properties as a result of the increasing hydrogenation of the carbon framework of C_{60} may be of interest for medicine, biology, and photonics. Unfortunately, the photophysical characteristics of the triplet state of $C_{60}H_{36}$ could not

be measured: the triplet–triplet absorption spectrum of this compound in the wavelength range accessible to measurements ($\lambda > 300$ nm) is lacking.

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Reactivity of terpenes and their analogues in an ‘organised medium’

N F Salakhutdinov, V A Barkhash

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Abstract. Published studies on the reactivity of terpenes and their analogues in an ‘organised medium’, viz. upon adsorption on solid catalysts and upon complex formation with cyclodextrins (photochemical processes), are analysed. It is shown that the use of an ‘organised medium’ not only improves the environmental characteristics of the known processes involving natural terpene derivatives. In addition, due to the specific features of the latter (conformational mobility, polyfunctionality), it opens broad opportunities for discovering unusual transformations, and this extends the prospects of using the ‘renewable raw materials’ for fine organic synthesis. The bibliography includes 92 references.

I. Introduction

‘Fixing’ of substrates through their adsorption on solid catalysts or due to complex formation with cyclodextrins are among the methods for influencing the reactivity of chemical compounds in thermal or photochemical processes that have been vigorously developing in recent years. This approach makes it possible to change sharply the selectivity of a process by creating steric hindrance in certain parts of the molecule or by imparting conformational rigidity to the molecule. In addition, adsorption of organic substrates on solid catalysts often changes the activation barriers to many transformations; in the case of molecules with multivariant reactivity, this makes it possible to direct the reaction along a previously unknown route.

Whereas reactions of aromatic compounds in the ‘fixed state’ have been intensely studied for a fairly long period,^{1,2} studies on the reactivity of terpenoids under these conditions are still at their early stage. However, it can be said with confidence that the number of works devoted to this topic will sharply increase, firstly, because researchers will attempt to extend the range of substrates that can be involved in these reactions and, secondly, because terpenoids are promising compounds, which can undergo new unusual transformations due to their polyfunctionality and conformational flexibility.

This review appears to be the first attempt to summarise the accumulated experimental results in this interesting field of organic chemistry.

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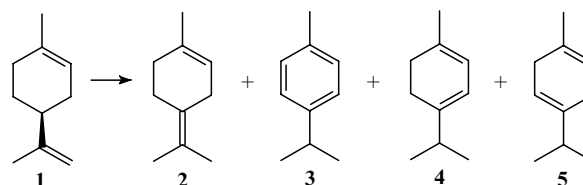
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II. Intramolecular reactions

1. Isomerisation of terpenoids on solid catalysts

Acid-catalysed rearrangements of terpenoids in various homogeneous media (from weakly acid to superacid) have been studied fairly comprehensively (see, for example, Ref. 3). In this Section, we consider the rearrangements of terpenoids on solid catalysts, which have been used with increasing frequency in recent years, in place of Lewis and Brønsted acids, for isomerisation of organic compounds.

Tanaka *et al.*⁴ have studied the transformations of limonene **1** in the presence of various metal oxides and phosphates at 60 °C under normal pressure.



Basic (MgO), acid-base (ZrO₂, Al₂O₃, and TiO₂–ZrO₂) and weakly acidic (AlPO₄, Nb₂O₅) catalysts proved to be inactive in this reaction. The other catalysts used in this study (including 96% H₂SO₄) led to the formation of mixtures of products containing terpinolene **2** (the main product) and **3–5** in various ratios.⁴ The SiO₂–Al₂O₃ and SO₄^{2–}/ZrO₂ systems proved to be the most active catalysts; the use of the latter results in fairly selective (up to 84%) formation of the compound **2**. The researchers believe that both Lewis and Brønsted acid sites are active in this reaction; however, better selectivity with respect to terpinolene is achieved in the case of catalysts having strong Lewis sites. At the same time, the strong solid Lewis acid SO₄^{2–}/Fe₂O₃ does not exhibit catalytic activity in this reaction, and this prompts the thought that the dependence of the degree of conversion of the compound **1** on the characteristics of the catalyst used is more complex.

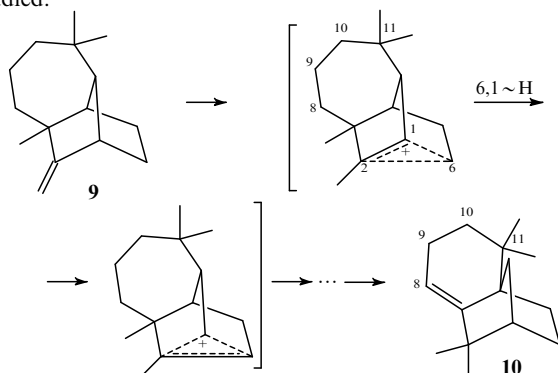
A number of patents^{5–10} have been devoted to isomerisation of α -pinene **6**, β -pinene **7** and turpentine containing these terpenes in the presence of X-type zeolites. This process leads to a mixture of products, which contains limonene **1** as the major component.



When this transformation is carried out at 150–175 °C, the yield of limonene amounts to 50%–65%; the reaction mixture also contains camphene **8** (15%–20%) and terpinolene **2**

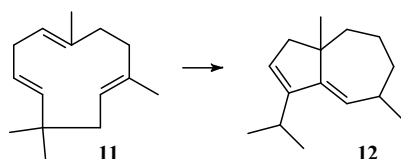
(~10%). It has been found¹¹ that the use of KX zeolite leads to better results than the use of the NaX, CaX and NH₄X zeolites.

The isomerisation of optically active longifolene **9** on the wide-pore β -zeolite giving optically active isolongifolene **10** has been studied.¹²

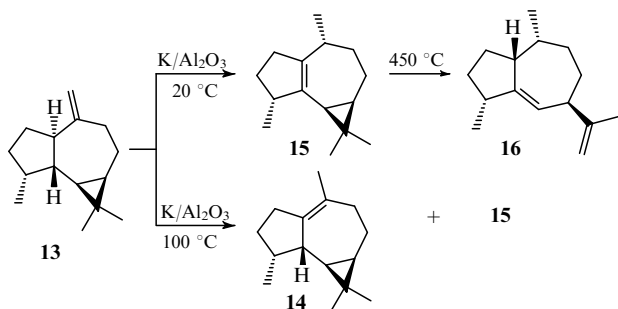


Polovinka *et al.*¹³ who have compared isomerisation on zeolites with transformations of the compound **9** in a superacid medium, have found that in the latter case, the degenerate rearrangement with 1,2-shift of the C(8)–C(11) bridge occurs more rapidly than the non-degenerate 6,1-hydride shift, and this gives the racemic compound **10**. Evidently, in the case where zeolite is used, the opposite relationship between the rates of these processes is observed, which results in the retention of the optical activity.

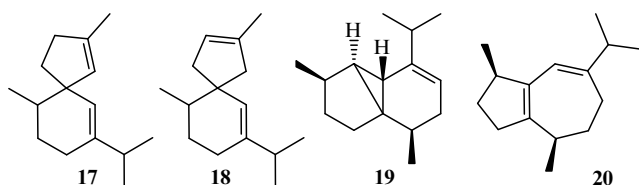
α -Humulene **11** also isomerises in the presence of β -zeolite: at 20 °C it is converted into bicyclohumulene **12** in 60% yield over a period of 1.5 h.¹⁴



When (+)-aromadendrene **13** is kept at room temperature over alumina with deposited potassium, it is converted quantitatively into (–)-isolekene **15**. If this reaction is carried out at 100 °C, (+)-ledene **14** is formed in addition to the compound **15**. The alkene **15** is thermally unstable and is converted into (+)- γ -gurjunene **16** on heating to 450 °C.¹⁵

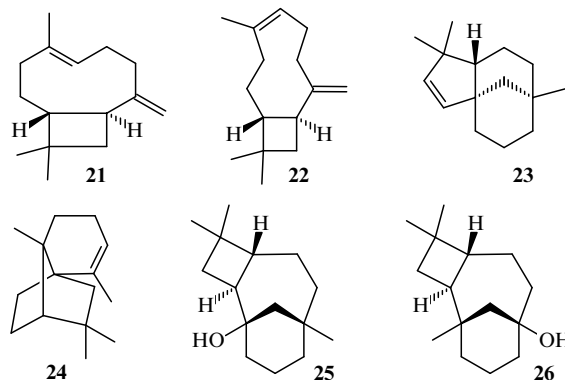


Isomerisation of the alkene **14** in the presence of the solid superacid SO₄^{2–}/TiO₂ (10 min, 20 °C) has led to 7-isopropyl-2,10-dimethylspiro[4,5]deca-1,6-diene **17** and its isomer, 7-isopropyl-2,10-dimethylspiro[4,5]deca-2,6-diene **18**.¹⁶ It was suggested that these compounds are formed intermediately during the more extensive isomerisation of ledene **14** in formic acid.

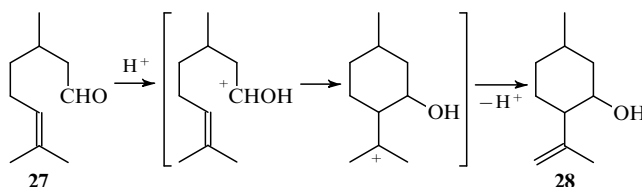


The same products were obtained in the isomerisation of (1*S*,4*R*,5*R*,6*S*,10*R*)-7-isopropyl-4,10-dimethyltricyclo[4.4.0.0^{1..5}]deca-7-ene **19**. It was found¹⁶ that the alkene **16** adsorbed on SO₄^{2–}/ZrO₂ isomerises at room temperature into (6*R*,10*R*)-3-isopropyl-6,10-dimethylbicyclo[5.3.0]deca-1(7),2-diene **20**.

The transformations of caryophyllene **21** and isocaryophyllene **22** on acid alumina lead mostly to clovene **23** and α -neoclovene **24**, respectively.¹⁷ Caryophyllene **21** not only isomerises to clovene **23** but is also hydrated to give alcohols, caryolan-1-ol **25** and isocaryolan-8-ol **26**.



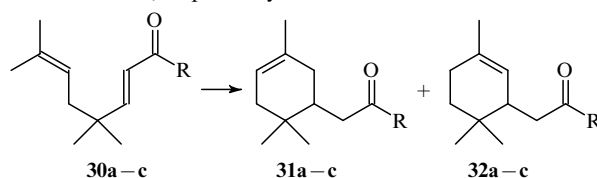
Considerable attention of researchers is paid to isomerisation of terpenoids containing functional groups, *i.e.* aldehydes, ketones, alcohols or epoxides of the terpene series. Cyclisation of citronellal **27** to isopulegol **28** in the presence of acidic zeolites such as clinoptilolite, mordenite and fojazit in various solvents at 61–84 °C has been studied.¹⁸ A possible mechanism of this process includes the protonation of the carbonyl group, the interaction of the carbocation centre with the 6,7-double bond and abstraction of a proton yielding the alcohol **28**.



The reaction mixture contains also a small amount of di(2-isopropenyl-5-methylcyclohexyl) ether **29** resulting from bimolecular dehydration of the alcohol **28**.

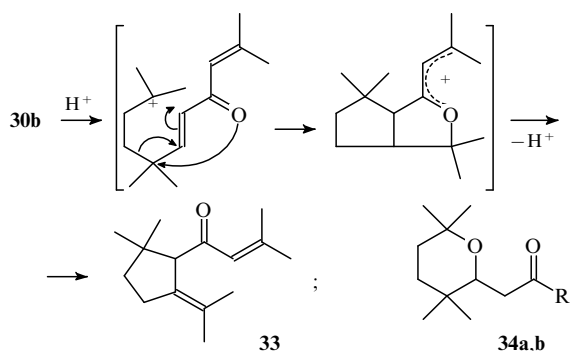
Salakhutdinov *et al.*¹⁹ have studied the behaviour of some dienones — analogues of terpene derivatives — on the NH₄Y- and β -zeolites in order to elucidate the dependence of the reaction route on the structure of the initial ketone and the reaction conditions.

The transformation of ketones **30a–c** in the presence of NH₄Y zeolite (60–80 °C) gives rise to mixtures of compounds **31a–c** and **32a–c**, respectively.

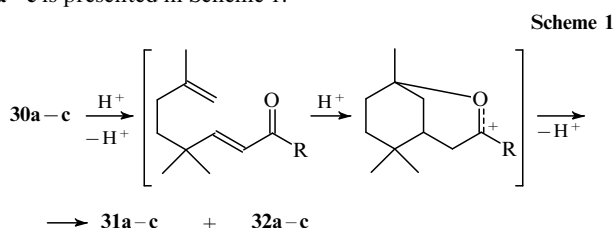


R = Me (a), CH=C(Me)₂ (b), Buⁱ (c).

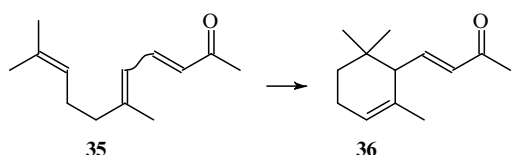
In the case of trienone **30b**, 3-isopropylidene-1,1-dimethyl-2-(1-oxo-3-methylbut-2-enyl)-cyclopentane **33** is formed, in addition to the compounds **31b** and **32b**. When the wide-pore β -zeolite is used as the catalyst and the substrate is adsorbed on the catalyst by a different method, the ketones **30a** and **30b** are converted into compounds **34a** and **34b**, respectively.



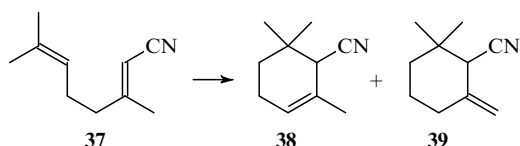
A possible mechanism of the transformations of the ketones **30a–c** is presented in Scheme 1.



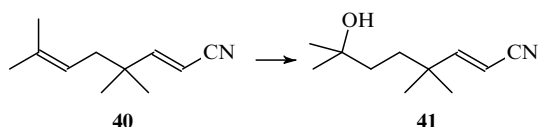
The use of the CaY zeolite made it possible to solve a problem of practical importance, namely, to carry out selective cyclisation of pseudoionone **35** to α -ionone **36**.



Cyclisation of 2,6-dimethyl-1,5-heptadienecarbonitrile has been reported.²¹ When this compound is applied on the β -zeolite at room temperature, it is converted almost immediately into cyclic nitriles **38** and **39**.

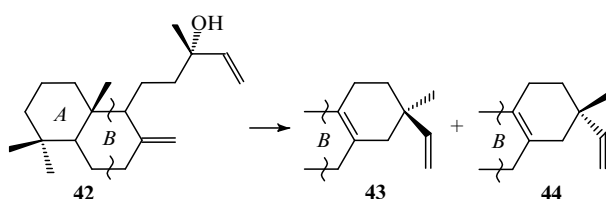


Prolonged keeping of nitrile **40** under the same conditions does not lead to any cyclic products; instead, the arising carbocation reacts with a nucleophile from the reaction medium to give alcohol **41**.



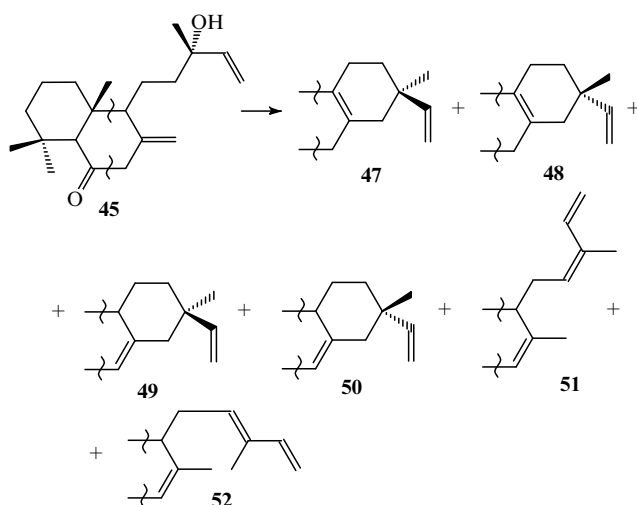
A study devoted to the transformations of labdane alcohols on the HY zeolite has been reported.²²

When epimanol **42** was kept on a zeolite (40 °C, 4.5 h), $\Delta^{8,9}$ -pimaradiene **43** and $\Delta^{8,9}$ -isopimaradiene **44** were isolated from the reaction mixture.

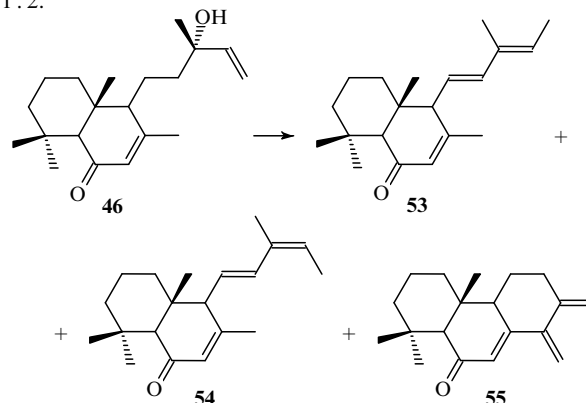


The transformations of 6-oxolarixol **45** on a zeolite gave bicyclic products **51** and **52**, in addition to tricyclic compounds

47–50. The bicyclic compounds could have formed *via* the migration of the 8,17-double bond to the position conjugated with the oxo-group, which makes cyclisation impossible.



Keeping compound **46**, the $\Delta^{7,8}$ -isomer of the oxalcohol **45**, on a zeolite leads to a mixture of products containing isomeric bicyclic ketones **53** and **54** and tricyclic ketone **55** in a ratio of 2:1:2.



Analysis of experimental data permitted the researchers cited²² to conclude that the transformations of the alcohols **42**, **45** and **46** on HY zeolite follow different pathways depending on the position of the double bond in ring *B*. In the case of the compounds **42** and **45** containing *exo*-methylene double bonds, acid-catalysed cyclisation yielding isomeric tricyclic diterpenoids occurs predominantly, whereas in the case of the compound **46** containing no highly reactive exocyclic double bond, the dehydration and polymerisation processes predominate.

A large number of works have been devoted to heterophase isomerisation of epoxides of the terpene series, which are fairly reactive compounds capable of being functionalised to alcohols, aldehydes and ketones.

Analysis of the data presented in Table 1 leads to the following conclusions. Firstly, in the presence of solid catalysts, apart from the cleavage of the epoxide ring and functionalisation of the substrate (for example, the transformations **60**→**61**; **62**→**63**+**64**; **87**→**88**), isomerisation of the carbon skeleton occurs (for example, **62**→**66**; **67**→**68**+**72**; **84**→**85**). Secondly, the use of various types of solid catalysts permits selective preparation from the same epoxide of products belonging to various classes. For example, limonene epoxide **62** can be converted either into ketone **61** or into aldehyde **66**, and α -pinene epoxide **67** affords either campholenic aldehyde **68**, or alcohol **70**, or the ketone **63**. Thus by varying the character of the catalyst used, one can control the reaction route. Thirdly, comparison of the products obtained from the epoxides under heterogeneous conditions (Table 1) with those formed in homogeneous acid media implies that isomerisation can follow

Table 1. Isomerisation of epoxides on solid catalysts.

The initial epoxide		The catalyst used	The main product		Ref.
Δ^2 -Carene epoxide 56		5A, 1010 AH, and 2020 AH zeolites	1,2-Dihydroperillic alcohol 57		23
Δ^3 -Carene epoxide 58		2020 AH zeolite	2-Methyl-5-isopropylcyclohexa-2,5-dien-1-ol 59		23
Isolimonene epoxide 60		HSZ-360-HUA zeolite	Carvenone 61		23
Limonene epoxide 62		ZnCl ₂ /KCl/NaCl salt melt	Carvone 63		24
			Isohydrocarvone 64		
		5A and 5Ca zeolites	Carvenone 61		25, 26
		3A, 4A, and 13X zeolites, TSZ-645-PSH1 + HCOOH	Dihydrocarvone 65		27
		3A, 4A zeolites	3-Isopropenyl-1-methylcyclopentane-1-carbaldehyde 66		28
α -Pinene epoxide 67a		Zeolites: HSZ-850, Na-mordenite, H- β , 3A, 4A, 13X, montmorillonite K-10 clay	Campholenic aldehyde 68		25, 29–32
α -Pinene epoxide 67b		Na-A zeolite, NaOH/Al ₂ O ₃	<i>trans</i> -Pino-carveol 69		31, 33
		F-9 zeolite + ClCCOOH, A4 zeolite	<i>trans</i> -Carveol 70		28, 34
		ZnCl ₂ /KCl/NaCl salt melts	Campholenic aldehyde 68		24
			Pinocarvone 71		
		H ₂ Cr ₂ O ₄ /Al ₂ O ₃	Carvone 63		34

Table 1 (continued).

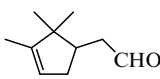
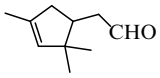
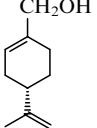
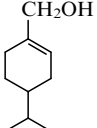
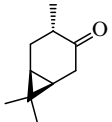
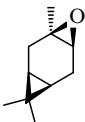
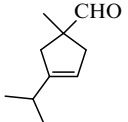
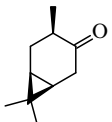
The initial epoxide		The catalyst used	The main product		Ref.
α -Pinene epoxide 67b		Tonsil LF-80 clay	Campholenic aldehyde 68		31
			Isocampholenic aldehyde 72		
		Al ₂ O ₃ /LiCl, Al ₂ O ₃	Pinocamphone 73		32, 33
β -Pinene epoxide 74a		HSZ-850-NAA zeolites, ZnX ₂ /KX/NaX salt melts (X = Cl, Br)	<i>cis</i> -Myrtanal 75		24, 35
		Zeolites: 3A, 4A, 13X, TSZ-645-PSHI + HCOOH	Perillic alcohol 76		27, 34
		3A and 4A zeolites	Phellandrol 77		26
			β -Pyronene 78		
β -Pinene epoxide 74b		NaOH/Al ₂ O ₃	<i>trans</i> -Myrtanol 79		33
		A-4 zeolite	<i>cis</i> -Myrtanol 80		34
<i>trans</i> -Epoxy-carane 81		Askanite–bentonite clay, β -zeolite, SiO ₂	3,3,6-Trimethylbicyclo[3.1.0]hexane-3-carbaldehyde 82		36, 37
		SO ₄ ²⁻ /ZrO ₂	"	"	37
			<i>trans</i> -Caranone 83		
<i>cis</i> -Epoxy-carane 84		SO ₄ ²⁻ /ZrO ₂	3-Isopropyl-1-methylcyclopent-3-ene-1-carbaldehyde 85		37
		SO ₄ ²⁻ /TiO ₂	<i>cis</i> -Caranone 86		

Table 1 (continued).

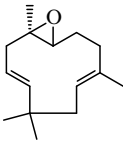
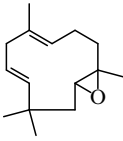
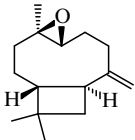
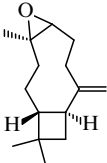
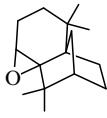
The initial epoxide		The catalyst used	The main product	Ref.
Humulene 6,7-epoxide 87		Al_2O_3 , $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3$	Humulenol 88	14, 38
		Askanite–bentonite clay	Humulen-7-one 89	14
Humulene 2,3-epoxide 90		Askanite–bentonite clay, $\text{SO}_4^{2-}/\text{ZrO}_2$	Humulen-2-one 91	14
Caryophyllene 4,5-epoxide 92		Al_2O_3	Caryophyllen-5-ol 93	38, 39
		TSZ-320-HUA zeolite	Dihydrocaryophyllen-5-one 94	40
		TSZ-320-HUA zeolite	Dihydroisocaryophyllen-5-one 95	40
		Al_2O_3	α -Betulenol 96	39
		3A, 4A, 13X, TSZ-320-HUA zeolites	Dihydroclove-9-ol 97	41
		Chromosorb W	4,10,10-Trimethyl-7-methylenebicyclo[6.2.0]-decane-4-carbaldehyde 98	42
Isocaryophyllene α -oxide 99		Al_2O_3	β -Betulenol 100	39
Isolongifolene epoxide 101		3A, 4A, 13X zeolites	Isolongifolan-4-one 102	40, 41
		"	Isolongifolan-4-ol 103	

Table 1 (continued).

The initial epoxide		The catalyst used	The main product	Ref.
Longifolene epoxide 104		A-4 zeolite	Longicamphenylone 105	41
1,8-Cineole 106		Zeolites: A-4, A-5 + HCOOH	α -Terpineol 107	43
1,4-Cineol 108		A-4 zeolite + Cl ₃ CCO ₂ H	β -Terpineol 109	43
		A-4 zeolite + HCOOH	α -Terpineol 107	43
Linalool epoxide acetate 110		3A zeolite	Karahanaenone 111	44

different pathways under homogeneous and heterogeneous conditions. For example, the transformation of humulene 6,7-epoxide **87** in a homogeneous acid medium follows a concerted mechanism with the consecutive participation of the 9,10- and 2,3-double bonds and with fixation of the most stable *cis-trans*-conformation,⁴⁵ whereas on solid catalysts, the isomerisation apparently occurs by a non-concerted mechanism, and a conformation other than the most stable is fixed. Depending on the nature of the catalyst, cleavage of the epoxide ring is followed either by 1,2-hydride shift to give ketone **89** (the askanite–bentonite clay) or by abstraction of a proton yielding alcohol **88** (SO₄²⁻/Al₂O₃).¹⁴

2. Photochemical isomerisation of terpenoids and their complexes with cyclodextrins

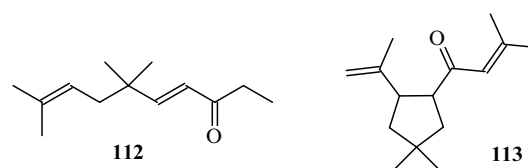
Besides thermal isomerisation of terpenoids in the presence of solid catalysts, considerable interest is aroused by photochemical transformations of these compounds; this is due to their natural origin and to the important role of solar light for the biogenetic processes.

Owing to polyfunctionality and conformational flexibility of terpenoids and to the high energy of UV radiation, exposure of solutions of terpenoids to radiation usually leads to non-selective transformations yielding numerous products. To increase the selectivity of the process, complex formation is employed. The formation of complexes with cyclodextrins (CD) makes the substrates conformationally rigid by fixing a particular arrangement of the reactive sites of the molecules. Consequently, photochemical processes either occur more selectively or follow a different pathway.

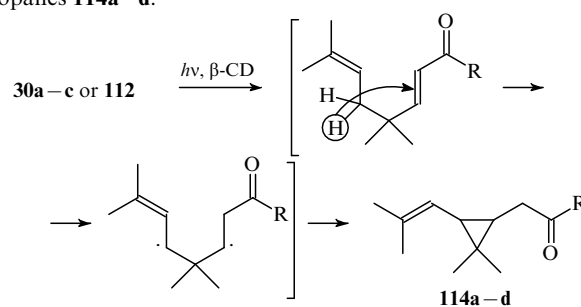
Cyclodextrins are natural cyclic oligosaccharides consisting of 6 (α -CD), 7 (β -CD) or 8 (γ -CD) D-(+)-glucopyranose units linked by α -1,4-glycosidic bonds. They are capable of acting as 'hosts' in complexes of the 'host–guest' type.² Cyclodextrins bind a guest molecule through hydrophobic interactions, *i.e.* by forming complexes with low-polarity molecules or parts of molecules. This complex formation closely resembles binding of substrates by

enzymes, which is especially valuable for the investigation of natural terpenoids. For example, complex formation with CD has been used^{2,46} to change the photochemical reactivity of organic molecules. However, these studies referred only to aromatic substrates.

In a study of photochemical reactions of compounds **30a–c** and **112** (the latter is a homologue of the dienone **30a**), it was found⁴⁷ that on exposure to radiation, the compounds **30a**, **30c** and **112** undergo *cis-trans* isomerisation, while the ketone **30b** is converted into cyclopentane derivative **113**.



The situation changes when complexes of the ketones **30a–c** and **112** with β -CD are irradiated. In all the cases, the allylic hydrogen atom undergoes a 1,4-shift to the carbon atom, located in the α -position with respect to the carbonyl carbon atom, and the 1,3-biradical undergoes ring closure to give substituted cyclopropanes **114a–d**.



R = Me (**a**), Buⁱ (**b**), CH₂CMe=CH₂ (**c**), Et (**d**) (**114**).

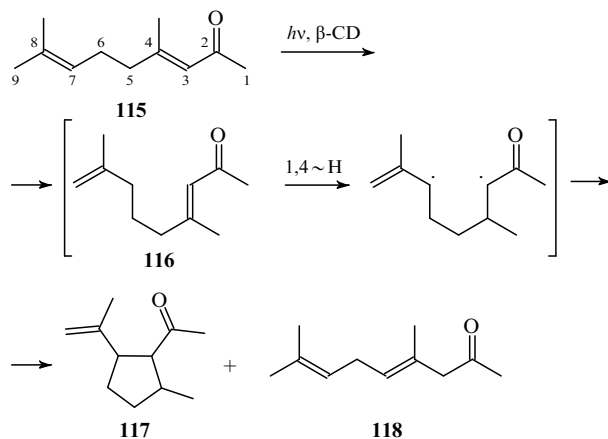
The results of the photolysis of the ketones **30a**, **30c** and **112** indicate that the size of the alkyl group **R** at the carbonyl carbon atom does not influence the direction of the process but does influence the yield of **114**: as the bulk of the alkyl substituent increases, the product yield decreases. Apparently, this is due to the fact that the complex formation between the substrates and β -CD becomes difficult.

Comparison of the photochemical reactions of the complexes of **30b** and **30c** with β -CD indicates that the presence of the rigid conjugated dienone system prevents the cyclisation with 1,4-shift of hydrogen yielding cyclopropanes (compound **30c**). The partial destruction of the dienone system due to allylic rearrangement facilitates transition to a conformation favourable for the cyclisation giving a cyclopropane ring.

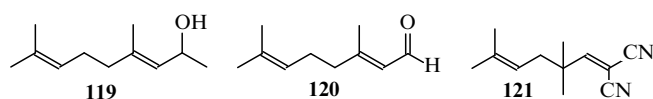
Analysis of the products resulting from the photochemical transformations of the ketone **30b** as such and as the complex with β -CD allowed Luzina *et al.*⁴⁷ to assume that the isopropylidene group of the ketone drops into the cavity of β -CD. This assumption is consistent with the fact that the allylic rearrangement occurring on irradiation of free **30b** involves the isolated double bond, whereas irradiation of the complex results in the violation of the conjugated system of π -bonds, which is substantially less favourable energetically. The assumption that the non-conjugated double bond is shielded is also in agreement with the fact that photochemical reactions of the complexes of **30a–c** and **112** with β -CD are always accompanied by *trans–cis*-isomerisation of the double bond.

The behaviour under the same conditions of a number of compounds containing a 2,6-dimethylhepta-1,5-dienyl fragment has been studied.²¹

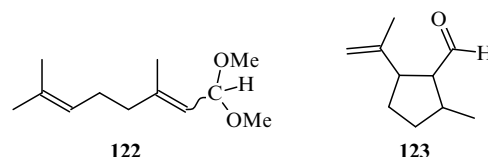
This seemingly insignificant modification of the structural unit results in substantial changes in the photochemical reactivity. In fact, when 4,8-dimethylnona-3,7-dien-2-one **115** is exposed to radiation, *trans–cis*-isomerisation of the double bond occurs. Irradiation of the complex of **115** with β -CD gives rise to cyclopentanone **117** and dienone **118** (*cf.* Refs 48 and 49).



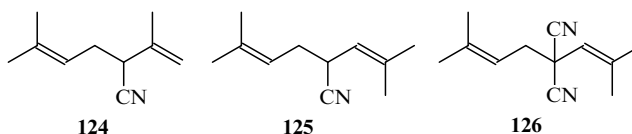
The influence of functional groups on the photochemical processes was studied²¹ in relation to alcohol **119**, aldehyde **120** and nitriles **37**, **40** and **121**.



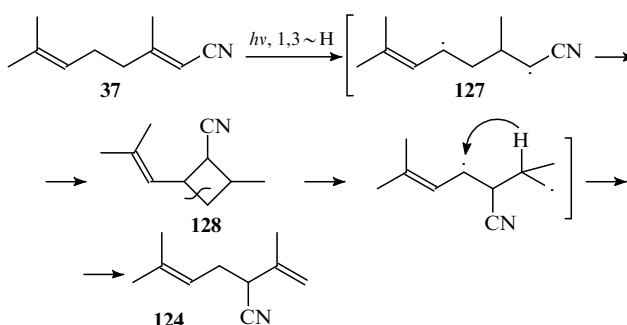
Neither the alcohol **119** nor its complex with β -CD exhibit photochemical activity indicating that the conjugated carbonyl group plays a significant role in this process. When citral **120** in methanol is exposed to radiation in the absence of β -CD, acetal **122** is formed, while this compound bound in the complex with β -CD is converted into cyclopentanone derivative **123** (*cf.* Ref. 49).



During irradiation of the nitriles **37**, **40** and **121**, cyclodextrin acts as a sensitizer. The reactions yield nitriles **124–126**, respectively.

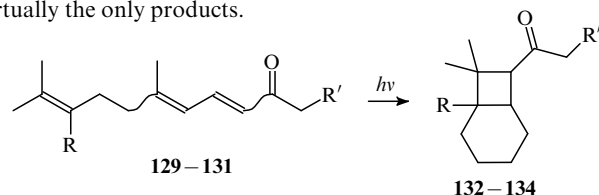


Let us consider a possible mechanism of the formation of these products using the nitrile **37** as an example.



The 1,3-hydride shift gives biradical **127**, which undergoes ring closure yielding nitrile **128** containing a cyclobutane ring. The subsequent rupture of the C–C σ -bond in the four-membered ring of the nitrile **128**, hydride shift and formation of a double bond give rise to the compound **124**.

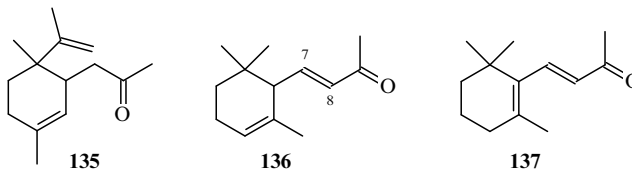
The irradiation of methanol solutions of the ketones: pseudoionone **129**, ϕ -ionone **130** and ϕ -methylionone **131**, the structures of which are similar to that of the ketone **115** and the carbonyl group is conjugated with two double bonds, results in *trans–cis* isomerisations of both double bonds. When solutions of complexes of the ketones **129** and **131** with β -CD are exposed to radiation, bicyclic ketones **132** and **134**, respectively, are formed as virtually the only products.



$R = R' = H$ (**129**, **132**); $R = Me$, $R' = H$ (**130**, **133**);

$R = H$, $R' = Me$ (**131**, **134**).

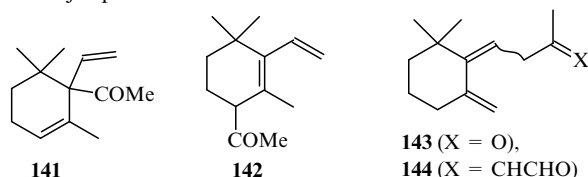
Photolysis of the complex of the ketone **130** with β -CD in solution follows a different pathway: bicyclic ketone **133** and ketone **135** ($\sim 1:1$, according to GLC) are formed as the main products.



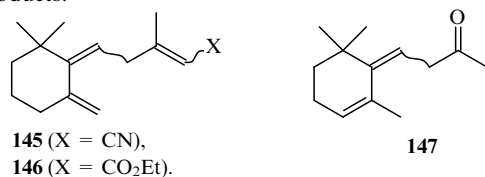
Photolysis of cyclic ionones — α -ionone **136**²¹ and β -ionone **137** and products of its crotonic condensation with acetaldehyde (**138**), acetonitrile (**139**), and ethyl acetate (**140**), has been studied.⁵⁰

The irradiation of a methanol solution of the ketone **136** and benzene solutions of the ketone **137** and the aldehyde **138** leads to

trans–*cis* isomerisation of the double bond. When the complex of **136** with β -CD is exposed to radiation, rearrangement products **141** and **142** are formed ($\sim 2:1$, according to GLC), while in the case of complexes derived from **137** and **138**, retro- γ -ionone **143** and retro- γ -ionylidenacetaldehyde **144**, respectively, are formed as the major products.



When β -ionylideneacetonitrile **139** and ethyl β -ionylideneacetate **140** are bound in complexes with β -CD, their reactivity does not change. Both these compounds themselves and their complexes with β -CD react to give compounds **145** and **146** as the main products.



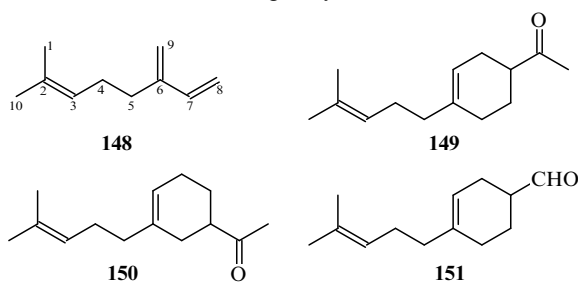
If the ketone **136** is bound in a complex with α -CD, this reaction yields retro- α -ionones **147**, instead of the compounds **141** and **142**.²¹

III. Intermolecular reactions

Intermolecular reactions of terpenoids in 'organised media' are of interest for both theoretical and applied organic chemistry. Multi-site adsorption of reactants and substrates on solid catalysts sharply decreases the activation barriers to a number of transformations, and hence, some practically valuable processes can be conducted at low temperatures and under atmospheric pressure. The fact that the adsorbed substrate and reagent molecules can approach each other and the presence of channels and pores in the catalyst not only decrease the activation energies of the possible processes but also provide the possibility of making a reaction follow selectively a particular pathway. This pathway is often unusual and unknown in the chemistry of homogeneous reactions. The use of solid catalysts (mostly aluminosilicates) in the chemistry of terpenoids leads sometimes to results that can change our views on the role of homology, isomerism and similarity of molecules.

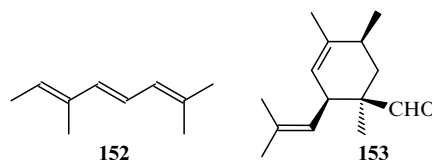
1. Cycloaddition reactions

Among cycloaddition reactions involving terpenoids, a special place belongs to the Diels–Alder reaction, because the adducts that are formed are used as perfumes or intermediates for their production. To carry out reactions of this type without a catalyst, high temperatures and elevated pressures are needed. Consequently, the reaction mixtures can contain substantial amounts of resins.⁵¹ The use of zeolite catalysts⁵² or chromatographic sorbents⁵³ in the reactions of a natural terpene, myrcene **148**, with methyl vinyl ketone and acrolein results in the formation of Diels–Alder adducts **149**–**151** in good yields under mild conditions.



The Cu²⁺NaY, NiNaX and dealuminised NiNaY' zeolites and natural clinoptilolite were used as catalysts in this reaction.⁵² It was found that the process is best performed without a solvent, at 50 °C using 1.5 moles of methyl vinyl ketone per mole of the triene **148** and 100% (by mass) of the NiNaX zeolite with respect to the organic components introduced in the reaction. Under these conditions, the degree of conversion of the compound **148** was 80% over a period of 5 h, and the overall yield of the products **149** and **150** was 45% (the **149**:**150** ratio was 9:1). In the presence of the CuNaY zeolite, the yield of the adducts **149** and **150** did not exceed 40%, their ratio being the same. The activity of natural clinoptilolite was the same as that of the NiNaX zeolite. When the reactions of the triene **148** with methyl vinyl ketone and with acrolein were carried out on the surface of a chromatographic adsorbent without a solvent, the reaction temperature could be decreased by 50–100 °C, and the adducts **149** and **151** were formed in good yields (73% and 66%, respectively).⁵³ The best effect was achieved when various kinds of silica gel for chromatography were used as the 'dry media'. Magnesium silicate was less active, and alumina was ineffective in this reaction. The catalytic effect of the sorbents was explained by the fact that the reactants, being adsorbed on them, lose their solvation shells, and this markedly facilitates the formation of pre-reaction complexes due to weak van der Waals interactions of the substrates.

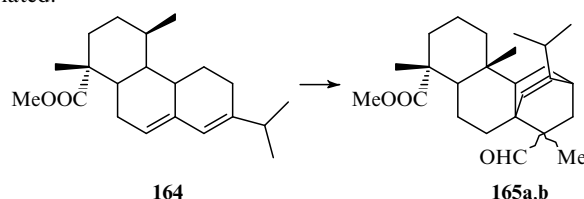
The possibility of stereoselective diene condensation of alloocimene **152** with α -methylacrolein in the presence of wide-pore β -zeolite has been demonstrated.⁵⁴



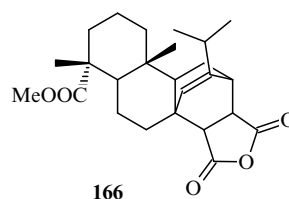
One of the four possible diastereomers, aldehyde **153**, is formed predominantly. Furthermore, it was found that other diastereomers do not isomerise into the compound **153** under the reaction conditions.

The results of the reactions of the trienes **148** and **152** with acrolein, methyl vinyl ketone, α -methylacrolein and crotonaldehyde on β -zeolite are presented in Table 2.

When the methyl ester of abietic ester **164** has been made to react with α -methylacrolein in the presence of wide-pore β -zeolite or askanite–bentonite clay (boiling benzene, 7 h), epimeric products of the Diels–Alder condensation **165a,b** have been isolated.⁵⁵



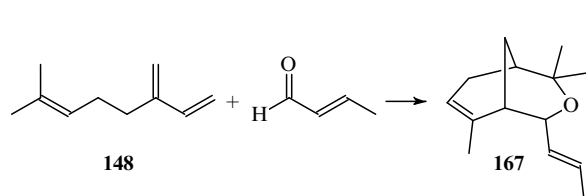
The reaction of the ester **164** with maleic anhydride on the same catalysts results in the formation of adduct **166**. In the absence of catalysts, the yield of the product **166** is five times lower, while the compounds **165a,b** are not formed at all.



The reaction of the triene **148** with crotonaldehyde carried out with the askanite–bentonite clay as the catalyst unexpectedly yielded 2,2,6-trimethyl-4-(prop-1-enyl)-3-oxabicyclo[3.3.1]non-6-ene **167** as the main product.⁵⁴

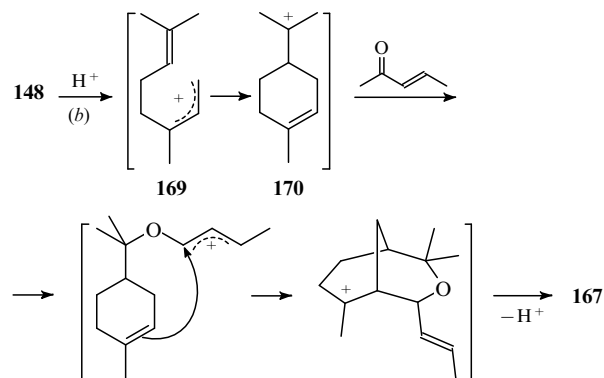
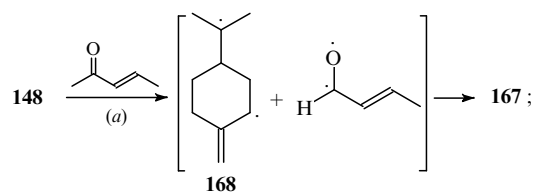
Table 2. Diels–Alder adducts obtained from the trienes **148** and **152** on a β type zeolite.⁵⁴

Diene	Dienophile	Adducts	Diene	Dienophile	Adducts
152	Acrolein	4,5 β -Dimethyl-2 β -(2-methylprop-1-enyl)-cyclohex-3-ene-1 β -carbaldehyde 154	148	α -Methyl-acrolein	Myrcenal 159
		4,5 β -Dimethyl-2 β -(2-methylprop-1-enyl)-cyclohex-3-ene-1 α -carbaldehyde 155		Methyl vinyl ketone	Isolone 160
	Methyl vinyl ketone	4,5 β -Dimethyl-2 β -(2-methylprop-1-enyl)-1 β -acetylcyclohex-3-ene 156		Croton-aldehyde	5 α -Methyl-1-(4-methyl-pent-3-enyl)cyclohex-1-ene-4 β -carbaldehyde 161
		4,5 β -Dimethyl-2 β -(2-methylprop-1-enyl)-1 α -acetylcyclohex-3-ene 157			5 β -Methyl-1-(4-methyl-pent-3-enyl)cyclohex-1-ene-4 β -carbaldehyde 162
148	Acrolein	Cyclonal 158			4 α -Methyl-1-(4-methyl-pent-3-enyl)cyclohex-1-ene-5 β -carbaldehyde 163



The formation of ether **167** is accompanied by transformation of three π -bonds into three σ -bonds and by the appearance of two new rings, *i.e.* this reaction conforms formally to the definition of the ‘Diels–Alder homo-reaction’. This type of transformation is unusual, because, despite the presence of conjugated double bonds in the molecule of **148**, it involves two non-conjugated double bonds, and because α,β -unsaturated aldehyde reacts at the carbonyl group rather than at the double bond, which would be the usual pathway.

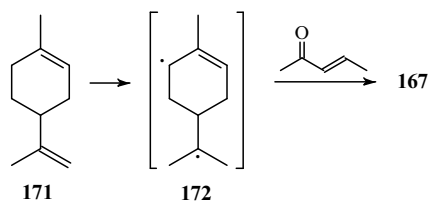
Let us dwell on the possible mechanisms of this unusual transformation. The researchers⁵⁴ proposed two mechanisms — homolytic (*a*) and heterolytic (*b*) mechanisms.



Both proposed mechanisms include the intermediate formation of compounds **168** and **170** with the *p*-menthane skeleton.

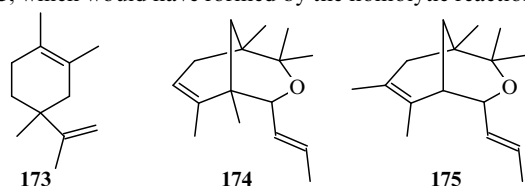
The same bicyclic ether **167** is formed in the reaction of diene **171** with crotonaldehyde. However, this reaction does not conform to the definition of Diels–Alder synthesis, because the diene **171** contains no conjugated double bonds, or to the definition of the Diels–Alder homo-reaction, since in this case only two double bonds disappear.

Since the formation of bicyclic ethers is of interest by itself, its mechanism has been studied in relation to the reaction of the diene **171** with various aldehydes. If the reaction of dipentene with crotonaldehyde occurs by the homolytic mechanism, one must assume that it involves the cleavage of the C(7)=C(8) double bond followed by hydride shifts to give the intermediate species **172**.

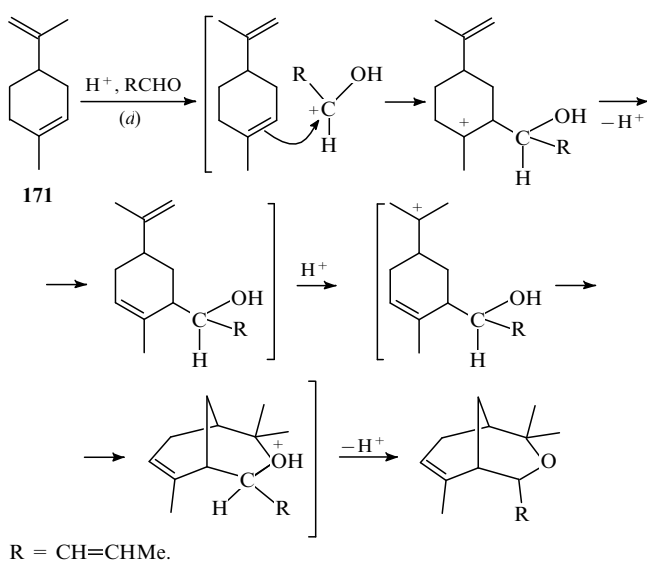
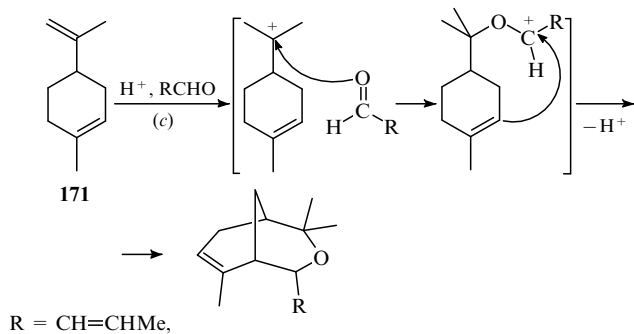


If the reaction follows the heterolytic mechanism, there is no need for the hydride shifts.

To make the choice in favour of a particular mechanism, a model compound, 4-isopropenyl-1,2,4-trimethylcyclohex-1-ene **173**, was introduced in the reaction with crotonaldehyde. The methyl group in the 4-position of this compound precludes the 1,2-hydride shifts leading to an intermediate structure like **172**. The reaction of the diene **173** with crotonaldehyde in the presence of the askanite–bentonite clay gave ether **174**; the positions of the methyl groups in this compound differ from those in compound **175**, which would have formed by the homolytic reaction route.



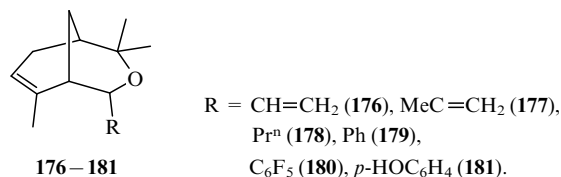
These facts count in favour of the heterolytic mechanism. The latter can be accomplished by two pathways.



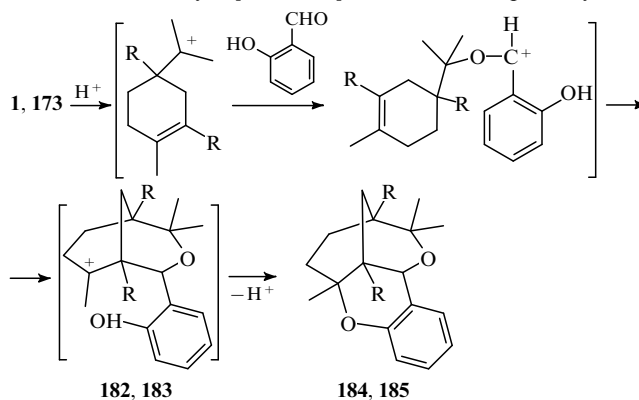
According to the first variant (pathway *c*), the protonated diene acts as the attacking species and the aldehyde acts as a nucleophile, whereas in the second variant (pathway *d*), the protonated aldehyde is an electrophilic species and the diene acts as a nucleophile. In our opinion, the fact that the reaction of 1-methylcyclohexene with crotonaldehyde, which models the first

step of pathway *d*, does not occur is evidence supporting the former pathway.

The reaction under consideration is general. Acrolein, α -methylacrolein, butyraldehyde, benzaldehyde, perfluorobenzaldehyde, and *p*-hydroxybenzaldehyde react with the diene **1** to give bicyclic ethers **176–181**, respectively.

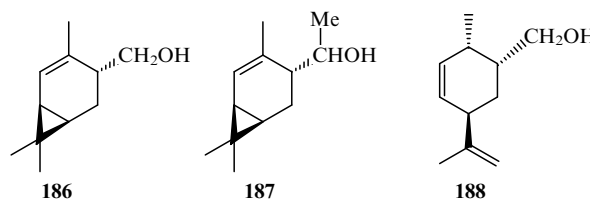


The formation of optically active ester **181** ($[\alpha]_{580}^{20} = +171.4^\circ$, c 5.49, CHCl_3) in the reaction of the diene **1** with *p*-hydroxybenzaldehyde also supports the heterolytic mechanism for this process.⁵⁶ At the same time, the reactions of the dienes **1** and **173** with salicylaldehyde, isomeric to *p*-hydroxybenzaldehyde, on the askanite–bentonite clay at room temperature do not stop at the stage of the formation of bicyclic ethers but proceed further to give compounds with the xanthene skeleton. Thus the interaction of the cationic centre in the intermediates **182** and **183** with the *o*-OH group gives rise to 2,2,8-trimethyl-3,7-dioxo-5,6-benzotricyclo[6.2.2.0^{4,12}]dodecane **184** and 1,2,2,8,12-pentamethyl-3,7-dioxo-5,6-benzotricyclo[6.2.2.0^{4,12}]dodecane **185**, respectively.⁵⁶



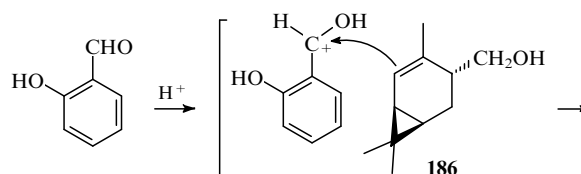
$R = \text{H}$ (**1**, **182**, **184**); Me (**173**, **183**, **185**).

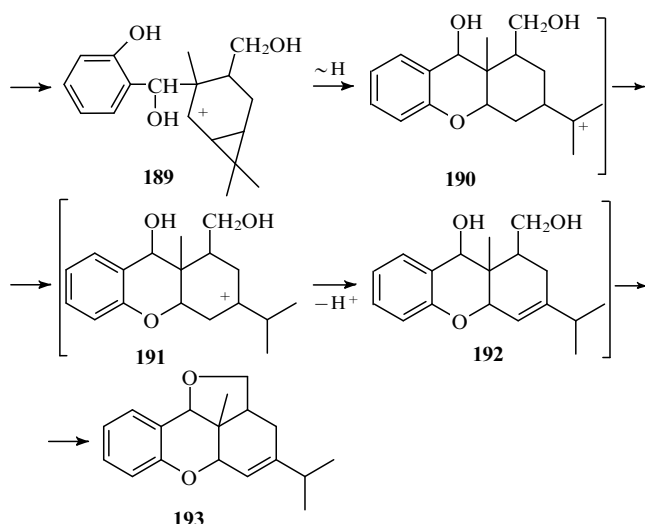
When salicylaldehyde was made to react with hydroxyalkenes of the carane and menthane series: valtherol **186**, *trans*-4-(1-hydroxyethyl)-2-carene **187** and (1*S*,4*R*,6*R*)-6-hydroxymethyl-*p*-mentha-2,8(9)-diene **188**



on the askanite–bentonite clay, products with the xanthene skeleton were also obtained, but in this case, this skeleton was fused to a tetrahydrofuran ring rather than to a tetrahydropyran ring as in **184** and **185**, and the arrangement of alkyl substituents was also different.

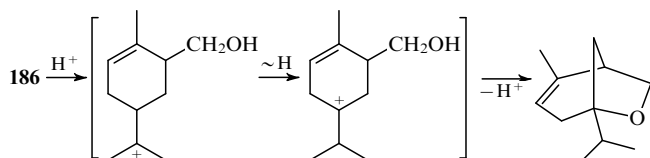
It is clear that in this case the process follows a different pathway.⁵⁷ A possible mechanism for this reaction is shown below in relation to valtherol.



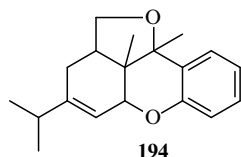


In the first step, protonated salicylaldehyde attacks the double bond of valtherol to give cation **189**. Intramolecular heterocyclisation in this cation accompanied by cleavage of the three-membered ring yields cation **190**. This can be followed by 1,2-hydride shift and deprotonation affording intermediates **191** and **192** and by heterocyclisation leading to the final product, 10-isopropyl-12-methyl-2,6-dioxo-3,4-benzotricyclo[6.3.1.0^{5,12}]-dodec-10-ene (**193**). The reactions of unsaturated alcohols **187** and **188** with salicylaldehyde apparently occur in a similar way.

A study of the behaviour of the unsaturated alcohols **186**–**188** in superacid media has shown⁵⁸ that under these conditions, the alcohols undergo intramolecular cyclisation yielding ethers with the oxabicyclo[3.2.1]octane skeleton.

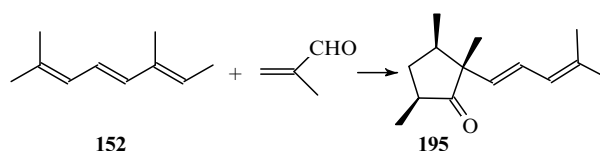


The researchers⁵⁸ suggested that the intramolecular cyclisation occurs upon the interaction of the carbocation centre with the hydroxyl group acting as an inherent nucleophile. When the reaction is carried out in the presence of the askanite–bentonite clay, the intramolecular cyclisation product of this type is formed only in the case of **187**, despite the fact that the entropy factor is favourable for this process. Apart from compound **194**, 1-isopropyl-4,6-dimethyl-7-oxabicyclo[3.2.1]oct-3-ene was isolated from the reaction mixture.⁵⁷ In other cases where the askanite–bentonite clay has been used, bimolecular reactions predominate.



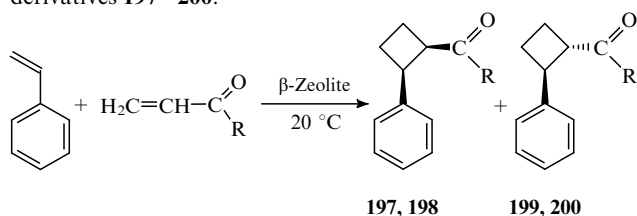
Comparison of the reactions of salicylaldehyde with the dienes **1** and **173** and with the unsaturated alcohols **186**–**188** shows that, although both processes afford xanthene derivatives, in the former case the protonated diene acts as an electrophile and the aldehyde is a nucleophile, while in the latter case, the protonated aldehyde reacts as an electrophile and the unsaturated alcohol is a nucleophile.

Interesting results have been obtained when alkenes have been made to react with compounds containing a vinyl or vinylidene group. An unusual reaction of the triene **152** with α -methylacrolein on the wide-pore β -zeolite has been reported.⁵⁴ The reaction occurs stereoselectively and yields substituted cyclopentanone **195**.



It is noteworthy that this reaction, which can formally be regarded as [3 + 2]-carbocyclisation with a 1,2-shift of the aldehyde proton, involves only one of the three double bonds of the triene **152**, while the two other bonds are incorporated unchanged in the ketone **195**. This fact stimulated Tatarova *et al.*⁵⁹ to search for monoalkenes that would enter into the same unusual reaction with α -methylacrolein. They found that of a broad range of alkenes including terpenes and model compounds, only styrene reacted with α -methylacrolein (β -zeolite, 20 °C). This reaction yields a mixture of diastereomers of 5-methyl-2-phenylcyclopentanone **196**.

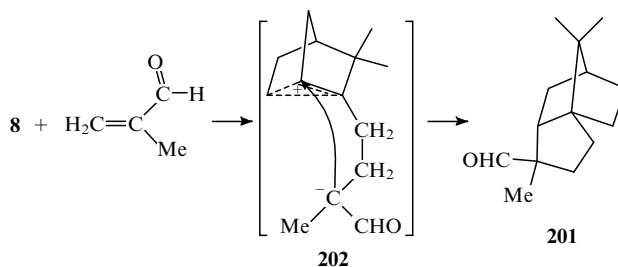
This process, like the reaction of α -methylacrolein with the triene **152**, occurs as [3 + 2]-carbocyclisation accompanied by a 1,2-shift of the aldehyde hydrogen atom. The reactions of styrene with methyl vinyl ketone and acrolein in the presence of the wide-pore β -zeolite result unexpectedly in the formation of cyclobutane derivatives **197**–**200**.⁵⁹



R = Me (**197**, **199**), H (**198**, **200**).

These reactions are among the best studied processes in the chemistry of photochemical transformations of unsaturated compounds and are referred to as 'cyclobutane reactions'. It is noteworthy that the formation of [2 + 2]-cycloaddition products from non-activated (or weakly activated) alkenes at room temperature is quite unusual. Thermal [2 + 2]-cycloaddition also occurs fairly rarely and is observed, as a rule, on prolonged heating of acetylene derivatives⁶⁰ or perhalogenated ethene derivatives.⁶¹

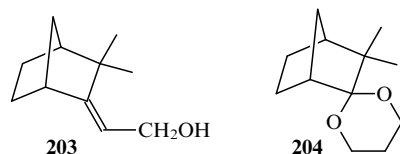
When α -methylacrolein reacts with camphene **8** which, like styrene, contains a terminal double bond but attached to the bicyclic framework, a cyclopentane fragment does form; however, the reaction pathway differs from that in the case of the triene **152**.⁵⁹ This reaction is accompanied by the rearrangement of the bicyclic skeleton and gives 4,10,10-trimethyltricyclo-[5.2.1.0^{1,5}]decane-4-carbaldehyde **201**.



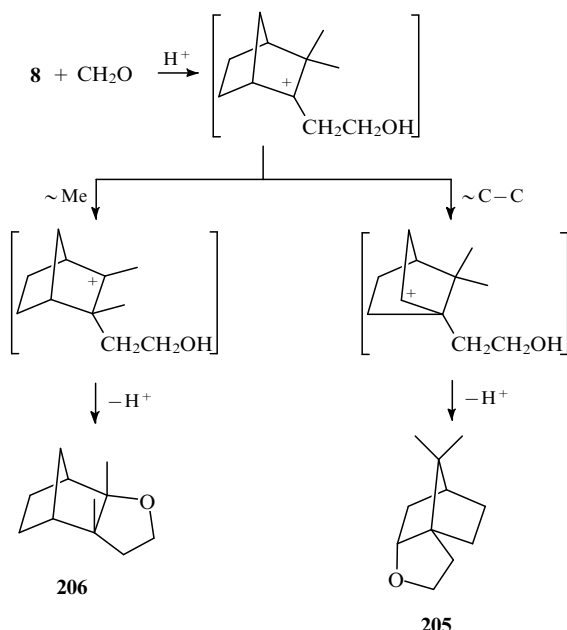
In this case, intermediate **202** is formed initially. Intramolecular stabilisation of the cationic centre results in a new carbocycle with an aldehyde group in the side chain.

The common feature of the reactions of α -methylacrolein with the compounds **152** and **8** is that [3 + 2]-carbocyclisation does occur in both cases. However, in the former case, it results from the transfer of a hydrogen atom, while in the latter case, it is due to the charge transfer. In the former case, the alkene acts as a dienophile and the aldehyde acts as a '1,3-dipole', while in the latter case, the aldehyde is a dienophile and the alkene is the '1,3-dipole' precursor.

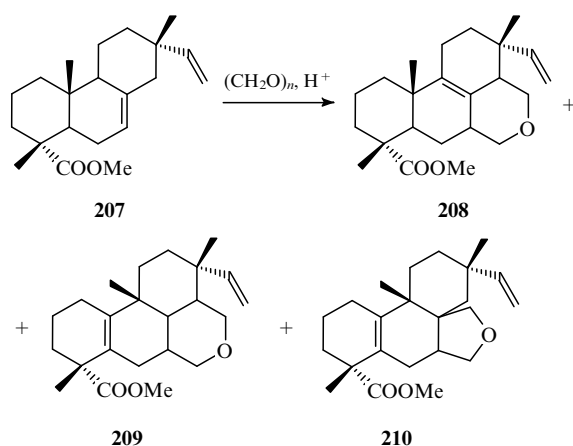
Now we consider the reaction of camphene **8** with formaldehyde on the wide-pore β -zeolite. The condensation of these compounds in the presence of acid catalysts (the Prins reaction)⁶² or in the presence of the KU-2 cation-exchange resin⁶³ yields mostly products with the non-rearranged camphene skeleton, namely 8-hydroxymethylcamphene **203** (or its ethers) and 1,3-dioxane **204**.



When this process is carried out on the β -zeolite, the formation of unusual products — tricyclic ethers **205** and **206** — becomes the main reaction pathway.⁵⁹ In the first stage, a protonated formaldehyde molecule attacks the C = C double bond in the compound **8**, and then the reaction follows two pathways: (1) Wagner–Meerwein rearrangement in which the positive charge is stabilised via binding to the oxygen atom (ether **205**); (2) 1,2-shift of the *exo*-methyl group followed by stabilisation of the arising cation (ether **206**).



A different variant of the Prins reaction, which is also unusual, is accomplished when methyl isopimarate **207** reacts with para-formaldehyde on the askanite–bentonite clay.⁶⁴



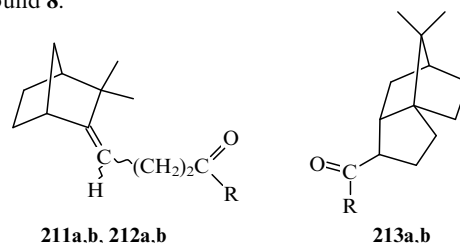
It was assumed that the products **208**–**210** are formed via successive addition of two equivalents of protonated formalde-

hyde to the initial ester **207**. The researchers noted that the reaction of the second formaldehyde molecule with the intermediate formed does not yield 1,3-dioxanes as would be the case in the classical variant of the Prins reaction or in the presence of other aluminosilicate catalysts.¹ Instead, it occurs again by the 'ene' mechanism giving rise to tetracyclic compounds with tetrahydropyran or tetrahydrofuran rings. During the reaction, 1,2-shift of the methyl group occurs, accompanied by the transformation of compounds of the pimarane series into rosane type compounds.

2. Addition reactions

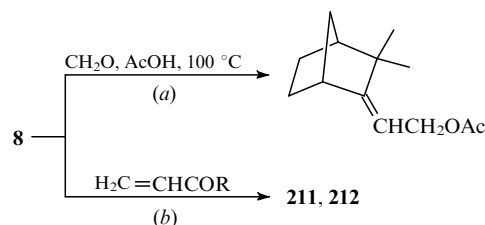
In this Section, we consider the addition reactions in which at least the main reaction pathway is not associated with cycloaddition.

The use of other carbonyl compounds, for example, acrolein or methyl vinyl ketone in place of formaldehyde, in the reaction with the alkene **8** results in the formation of only slight amounts of carbocyclisation products **213a,b**. Compounds **211** and **212** formed as mixtures of geometrical isomers are the major products in this case. These compounds can formally be regarded as resulting from replacement of the vinylic hydrogen atom in compound **8**.

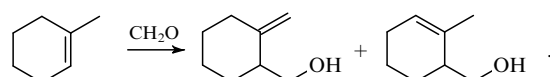


R = H (a), Me (b).

Judging from the structures of the main products, the reaction under consideration resembles most closely two well known processes: the 'ene' reaction and the Prins reaction; however, it differs from these reactions in some significant points. According to the definition proposed by Snider,⁶⁵ an 'ene' reaction is the interaction of an alkene having an allylic hydrogen atom (the 'ene') with a compound containing a double or a triple bond (the 'enophile') with the formation of a new bond accompanied by the migration of the double bond in the 'ene' and by the 1,5-hydrogen shift. In the reaction under consideration, alkene **8** acts as the 'ene' having an allylic hydrogen, while acrolein or methyl vinyl ketone acts as the 'enophile'. The interaction yields two σ -bonds (C–C and C–H); no double bond migration or 1,5-shift of the allylic hydrogen occurs. Thus, the reaction in question does not conform to the definition of the 'ene' reaction. Now we compare this transformation of the alkene **8** with the Prins reaction.



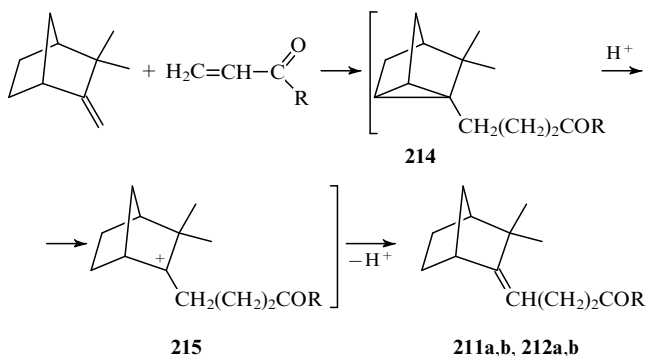
The Prins reaction (pathway *a*) consists in the interaction of a protonated aldehyde (which is $\text{H}_2\text{C}^+\text{OH}$ virtually in all cases) with a double bond resulting in the transformation of the carbonyl group into an alcohol group or into the corresponding ether. If the reaction of an alkene with formaldehyde is carried out thermally without a catalyst, it affords products of 'ene' synthesis, for example



When carbonyl compounds are made to react with the alkene **8** in the presence of a zeolite, the β -olefinic atom attacks initially

the polarised double bond, and the carbonyl group remains intact. Thus, this process cannot be classified as the Prins reaction. This type of reaction could be referred to as 'pseudo-ene synthesis'.

Now we consider a possible mechanism of the 'pseudo-ene synthesis'. For example, the process can occur as a sequence of transformations with the intermediate formation of tricyclic derivative **214**.

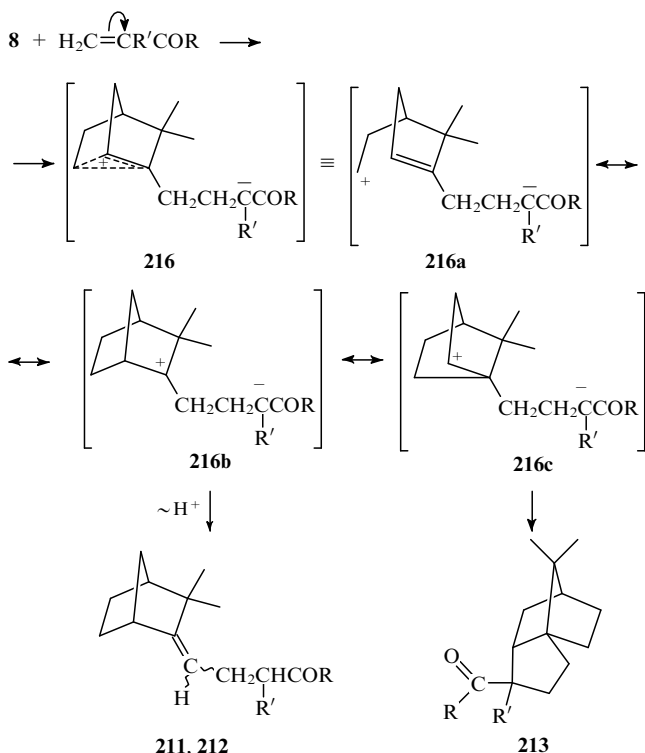


R = H, Me.

Reactions of this type have been reported previously;⁶⁶ however, the tricyclic product described in this study was converted into a bicyclic compound only on refluxing in AcOH.

Thus if we assume that the reaction occurs via the intermediate **214**, we should expect the formation of tricyclic products. However, this is not the case.

Probably, the reaction under consideration occurs via the intermediate formation of non-classical ion **216**:



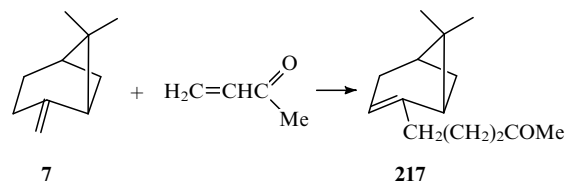
R = R' = H (a), R = Me, R' = H (b).

R = H, R' = Me.

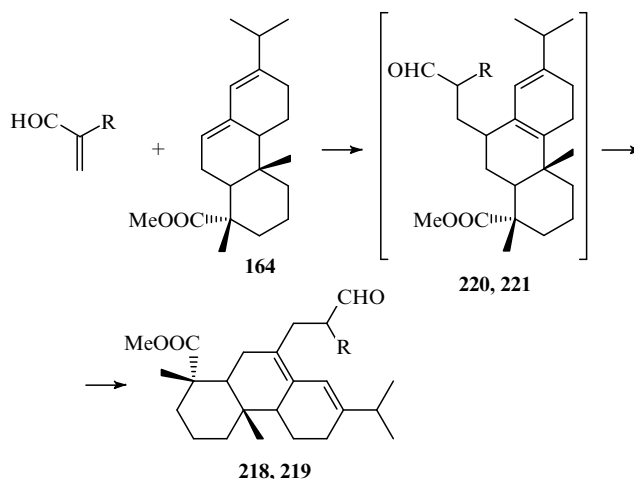
This ion can be represented as the set of resonance structures **216a**–**216c**, which can undergo either carbocyclisation (**216c**→**213**) or formation of a double bond (**216b**→**211, 212**). The relationship between these routes is governed by the nature of the substituent R'.

When aluminosilicate catalysts are used in reactions of enophiles with alkenes in which the allylic hydrogen atom is more mobile than that in **8**, typical products of the 'ene' reaction are

formed. For example, it has been reported⁵⁹ that the reaction of alkene **7** with methyl vinyl ketone on the β -zeolite gives rise to 6,6-dimethyl-2-(4-oxopentyl)bicyclo[3.1.1]hept-2-ene **217**.

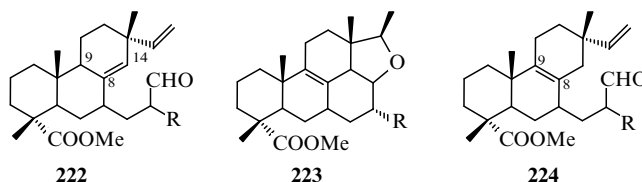


The reaction of the compound **164** with acrolein or α -methylacrolein in the presence of the β -zeolite gives compounds **218** and **219**, which result from isomerisation of the products of the ene synthesis **220** and **221**.⁵⁵



R = H (**218, 220**), Me (**219, 221**).

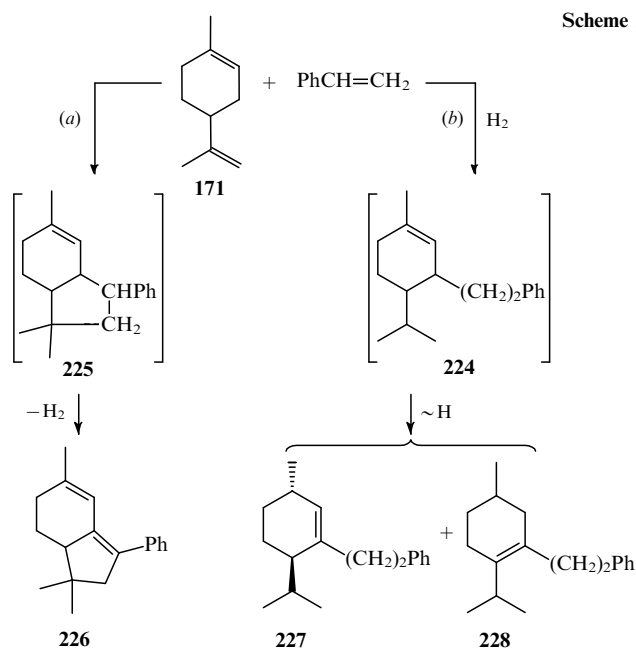
Methyl isopimarate **207** containing one endocyclic C = C bond and two allylic hydrogen atoms in the 9- and 14-positions reacts with acrolein or α -methylacrolein in the presence of the β -zeolite or askanite–bentonite clay according to two competing pathways: $\Delta^{8,9}$ - and $\Delta^{8,14}$ -ene condensation,⁶⁷ the latter being the predominant pathway. Under the reaction conditions, the product of $\Delta^{8,14}$ -condensation **222** undergoes further transformations, namely, intramolecular reaction of the aldehyde group with the double bond followed by cyclisation of the resulting alcohol to ether **223** with a new type of skeleton. The product of $\Delta^{8,9}$ -condensation **224** is more stable under the reaction conditions and undergoes no secondary transformations, although it is formed in substantially smaller amounts.



R = H, Me.

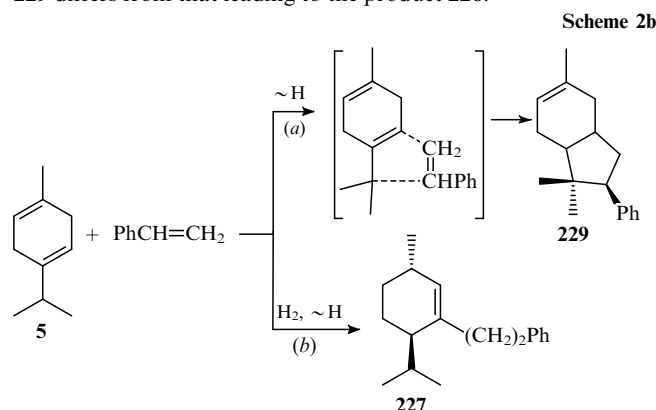
Interesting results have been obtained when styrene has been involved in the reaction with the terpenes **171** and **5**, containing no carbonyl group, on the askanite–bentonite clay. The reaction of the diene **171** with styrene at room temperature leads to a mixture of products **226**, **227** and **228** in a ratio of 1.5 : 1 : 3 (Scheme 2a).

The bicyclic compound **226** is probably formed via dehydrogenation of the intermediate **225**, which can be formally regarded as resulting from [3C+2C]-cycloaddition. The compounds **227** and **228** can be regarded as the products of alkylation and hydrogenation of **171** to give the intermediate **224** which then



undergoes allylic rearrangements. The workers⁵⁹ have noted that in the presence of clay, the diene **171** does not react with styrene derivatives containing electron-withdrawing (*p*-nitrostyrene, *p*-bromostyrene, 2,3,4,5,6-pentafluorostyrene) or electron-donating (*p*-methylstyrene) substituents. Apparently, the influence of substituents is mostly due to the steric restrictions to the adsorption of the substrate on a catalyst created by them rather than by their electronic effects.

The interaction of styrene with the diene **5** also affords a mixture of products: alkene **228**, bicyclic compound **229** and *p*-cymene (Scheme 2b). It is noteworthy that the mode of coupling of the molecules of styrene and **5** giving rise to compound **229** differs from that leading to the product **226**.

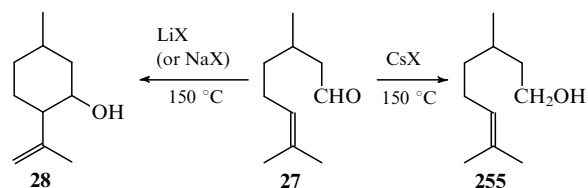


It is also noteworthy that the processes of hydrogenation and dehydrogenation of the alkenes **171** and **5** occur at room temperature. In fact, hydrogenation of alkenes is usually carried out in the presence of zeolite catalysts doped with metals such as Pt, Pd or Ru at 100–200 °C, while dehydrogenation is performed with the same catalysts at 400–600 °C.¹

Considerable attention of researchers has been paid to the hydration of terpenoids with various hydroxyl-containing reagents on aluminosilicate catalysts. The catalysts used for this purpose and the products thus obtained are listed in Table 3. Analysis of the results of these reactions indicates that hydration of terpenoids is accompanied by rearrangements, by oxidation of the alcohols formed initially and by the formation of ethers from these alcohols.

Replacement of the aluminium alkoxide in the Meerwein–Ponndorf–Verley reaction by zeolites leads to reduction of the

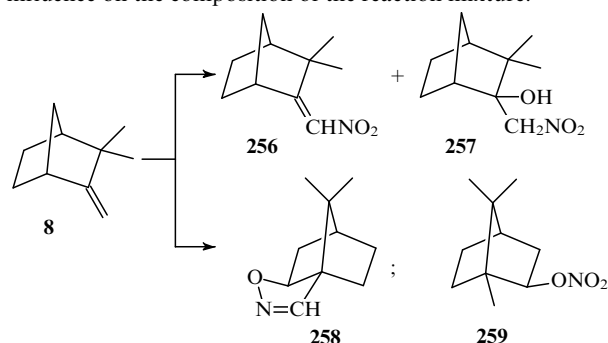
aldehyde **27** either to the cyclic alcohol **28** or to acyclic citronellol **255**, depending on the catalyst used.⁷⁷



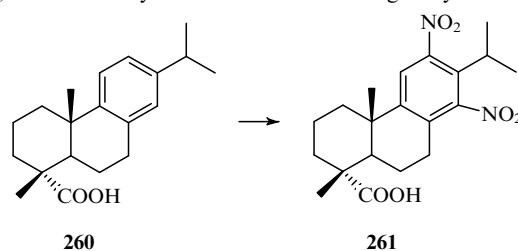
However, in the presence of zeolites, **27** cyclises to **28** (see Ref. 18) and, in all probability, it is more correct to regard this reaction, carried under the conditions described,⁷⁷ as carbocationic cyclisation rather than as the Meerwein–Ponndorf–Verley reaction.

The nitration of camphene **8** with N_2O_4 or with 69% HNO_3 in the presence of various zeolite catalysts has been studied.⁷⁸

It was shown⁷⁸ that when N_2O_4 is used, depending on whether or not a catalyst is present and on the type of the solvent, the reaction occurs either as nitration to give ω -nitrocamphene and 2-hydroxy-3,3-dimethyl-2-nitromethylnorbornane **257** or as nitrosation followed by rearrangement of the camphene skeleton and by intramolecular cyclisation yielding 10,10-dimethyl-3-aza-4-oxatricyclo[5.2.1.0^{1,5}]dec-2-ene **258**. Variation of the nature of the zeolite basically does not change the reaction outcome. When camphene **8** reacts with 69% HNO_3 , isobornyl nitrate **259** is formed as the major product; the addition of a zeolite has virtually no influence on the composition of the reaction mixture.

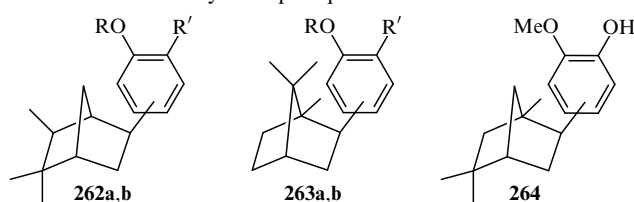


The nitration of dehydroabietic acid **260** in the presence of acidic montmorillonite impregnated with copper nitrate affords 12,14-dinitrodehydroabietic acid **261** in a good yield.⁷⁹



Now we consider arylation and alkoxylation of terpenoids on aluminosilicate catalysts. This group of reactions is very significant, because many of the products obtained in this way are used as intermediates for the production of perfumes.⁸⁰

When camphene **8** is arylated with phenols using the askanite clay as the catalyst, the composition of the reaction mixture depends on the reaction temperature.⁸¹ At 160–180 °C, the mixture consists only of terphenols **262**–**264**.

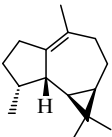
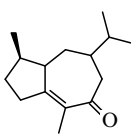
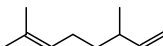
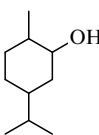
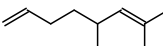
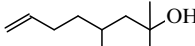
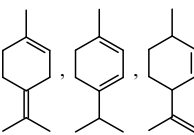
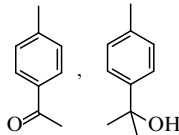
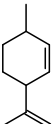
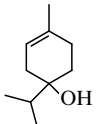
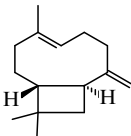
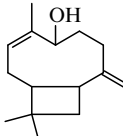
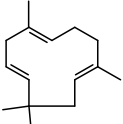
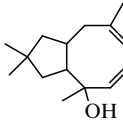


$\text{R} = \text{R}' = \text{H}$ (a); $\text{R} = \text{Me}$, $\text{R}' = \text{OH}$ (b).

Table 3. Hydration of terpenoids on solid catalysts.

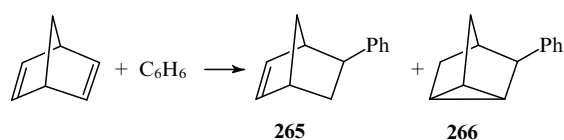
Terpenoid		The catalyst used	Reaction products		Ref.
Norbornadiene 230		H-Ultrasil	Nortricyclen-3-ol 231		68
			5- <i>exo</i> -Hydroxynorborn-2-ene 232		
		NdNaY zeolite	Ether 233		68
			Ether 234		
α -Pinene 6		GO-82 zeolite	Borneol 235a		69
		3A, 4A, 13X zeolites + Al(OH) ₃ , HSZ-710-HOA	α -Terpineol 107		70, 75
β -Pinene 7		2020AM zeolite	<i>trans</i> -Verbenol 236		70
Camphene 8		HSZ-600-HOA zeolite + CuCl ₂	Isoborneol 235b		70
Limonene 1		3A and 4A zeolites	α -Terpineol 107		70
		HSZ-710-HOA zeolite	Carvone 63		70
Tricyclene 237		HSZ-640-HOA zeolite + Cu(OH) ₂	Isoborneol 235b		70
Isolongifolene 10		HSZ-600-HOA zeolite	9-Oxoisolongifolene 238		71
α -Cedrene 239		HSZ-600-HOA zeolite	α -Cedranone 240		72
Longicyclene 241		2020AH zeolite	Longicamphene hydrate 242		73
Longipinene 243		HSZ-600-HOA zeolite	Longiverbenone 244		73

Table 3 (continued).

Terpenoid	The catalyst used	Reaction products	Ref.
(+)-Ledene 14 	Various zeolites + Ni(OH) ₂	3-Isopropyl-6,10-dimethyl-bicyclo[5.3.0]dec-6-en-5-one 245 	73
Dihydro-myrcene 246 	HSZ-620-HOA zeolite + Al(OH) ₃	Carvomenthol 247 	74
5,7-Dimethyl-1,6-octadiene 248 	HSZ-640-HOA zeolite + CHCl ₂ COOH	2,4-Dimethyloct-7-en-2-ol 249 	74
Terpinolene 2 , α -Terpinene 4 , Isolimonene 250 	HSZ-320-HOA, HSZ-600-HOA zeolites	<i>p</i> -Methylacetophenone 251 , 2-(<i>p</i> -Tolyl)-propan-2-ol 252 	75
Isolimonene 250 	HSZ-640-NAA zeolite	Terpinen-4-ol 253 	75
Caryophyllene 21 	3A, 4A zeolites	Caryophyllen-5-ol 93 	
α -Humulene 11 	H-zeolites	2,6,10,10-Tetramethylbicyclo[6.3.0]undeca-3,5-dien-2-ol 254 	76

When the temperature is decreased to 100 °C, the reaction mixture contains up to 60% of terpenophenyl ethers. The terpenophenol fraction consists mostly of *o*-terpenophenols, the terpene residues of which have the isocamphyl structure (**262a**, 74%) or isobornyl structure (**263a**, 26%). In some studies,^{81–84} in addition to the traditional acid catalysts (Lewis and Brønsted acids), the askanite clay was also used for arylation of various terpenes. In each case, a broad range of compounds have been obtained. This was explained by secondary rearrangements of labile terpene skeletons, by dearylation, and by possible attack at various positions of the aromatic ring by the arising bicyclic carbocations. For example, when the alkene **8** condenses with guaiacol, the reaction mixture contains products **264** with the isofenchyl skeleton, together with the compounds **262b** and **263b**.

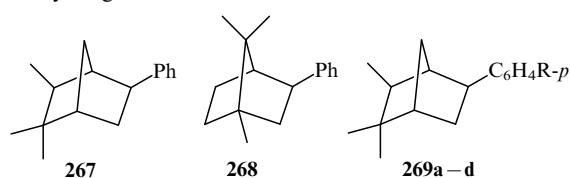
Arylation of terpenes and model compounds has been carried out on zeolite catalysts. For example, phenylation of norbornadiene **230** on wide-pore and medium-pore zeolites has been described.⁸⁵

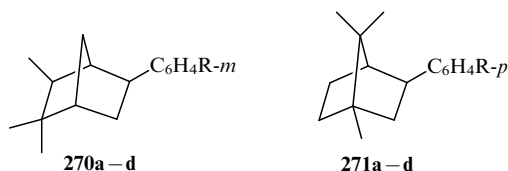


In the presence of wide-pore zeolites, 5-phenyl-2-norbornene **265** and 3-phenylnortricyclene **266** were obtained; medium-pore catalysts proved to be inactive in this reaction. Arylation of 1- and 2-methylnorbornenes with aromatic hydrocarbons in the presence of the TsEOKAR-2 zeolite-containing catalyst has been reported.⁸⁶ This reaction gave a mixture of hydrocarbons of unknown structures.

Arylation of camphene **8** with benzene and its mono- and disubstituted derivatives in the presence of the wide-pore β -zeolite has been investigated.⁸⁷

The reaction of benzene with optically active camphene yields racemic products **267** and **268**, the former compound predominating. Attention is attracted by the unusual structure of the terpene skeleton in the compound **268** with the methyl groups at the 1-, 4-, and 7-positions. For this skeleton to be formed, at least a five-stage rearrangement of the arising camphenyl cation must occur; therefore, the researchers⁸⁷ put forward the hypothesis that the carbocations generated from camphene on zeolites possess relatively long lifetimes.

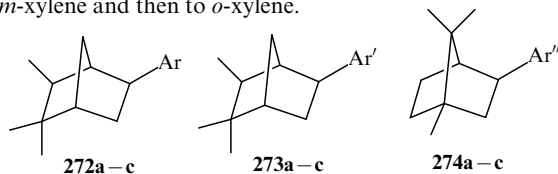




R = Me (a), Et (b), Prⁿ (c), Bu^t (d).

Analysis of the reaction mixtures obtained by the reaction of the alkene **8** with monoalkyl-substituted benzene derivatives indicates that as the size of the alkyl substituent increases, the overall yield of products diminishes from 60% (**269a–271a**) to 20% (**269d–271d**). The proportion of the meta-isomer **270a–d** in the mixture increases with an increase in the bulk of the alkyl group. Monosubstituted benzene derivatives containing electron-donating groups other than methyl (phenol, anisole) or electron-withdrawing groups (nitrobenzene, benzaldehyde, chlorobenzene) do not enter into the reaction with camphene **8** on the β -zeolite.

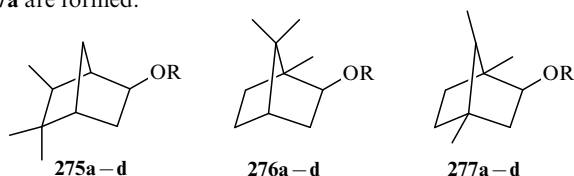
Isomeric xylenes give rise to products **272–274**, the overall yield of the reaction products increasing on passing from *p*-xylene to *m*-xylene and then to *o*-xylene.



Ar = 2,5-Me₂C₆H₃ (**272a**), 2,4-Me₂C₆H₃ (**272b**), 3,4-Me₂C₆H₃ (**272c**);
 Ar' = 2,5-Me₂C₆H₃ (**273a**), 2,6-Me₂C₆H₃ (**273b**), 2,3-Me₂C₆H₃ (**273c**);
 Ar'' = 2,5-Me₂C₆H₃ (**274a**), 2,4-Me₂C₆H₃ (**274b**), 3,4-Me₂C₆H₃ (**274c**).

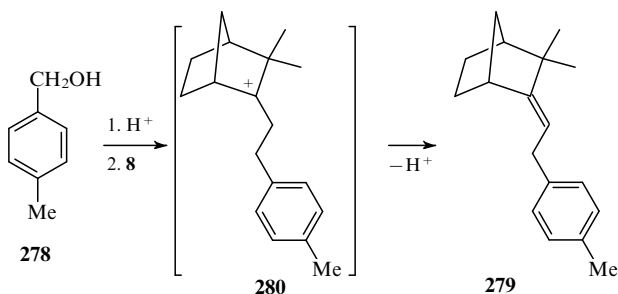
Mesitylene does not react with camphene. Naphthalene and biphenyl also do not enter into this reaction, although their successful alkylation with lower alkenes in the presence of zeolites has been reported in a vast number of studies (see, for example, Ref. 88).

When benzyl alcohol reacts with the alkene **8** on the β -zeolite, alkoxylation occurs instead of arylation, and the ethers **275a–277a** are formed.



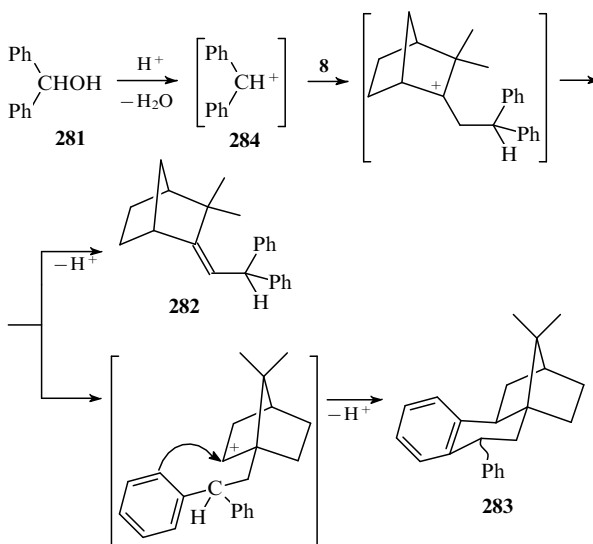
R = CH₂Ph (a), CH₂CH₂Ph (b), CH₂C₆H₄Me-*m* (c), Me (d).

Phenethyl alcohol reacts with the alkene **8** in the presence of the β -zeolite to give the ethers **275b–277b**. The introduction of strong electron-donating (*p*-methoxy) or strong electron-withdrawing (*p*-nitro) substituents into the aromatic nucleus of benzyl alcohol retards alkoxylation. However, *m*-methylbenzyl alcohol is readily converted into the ethers **275c–277c**. The reaction involving *p*-methylbenzyl alcohol **278** requires much more rigorous conditions and follows another route yielding hydrocarbon **279**.



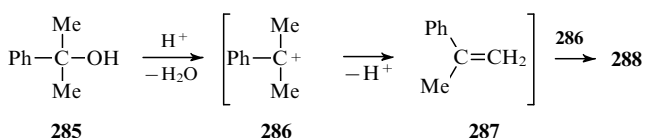
The study of the reactions of camphene with *p*- and *m*-methylbenzyl alcohols showed that minor changes in the structure of the reactant result in an absolutely different reaction pattern. This fact cannot be explained by merely the different thermal effects of formation of *p*- and *m*-methylbenzyl cations from the corresponding alcohols and of the camphenyl cation from the alkene **8**, because the difference between the energies of formation of the methylbenzyl cations is relatively small.

It may be expected that the transition from benzyl alcohol to benzhydrol would lead to *C*-alkylation instead of *O*-alkylation. In fact, the reaction of benzhydrol **281** with the alkene **8** yields hydrocarbons **282** and **283**.⁸⁹



Apparently, in the reaction of the alkene **8** with the alcohol **281**, it is the benzyl cation **284** arising from the alcohol **281** upon protonation and dehydration that acts as the electrophilic species, and not the camphenyl cation, as in the reaction of **8** with benzyl alcohol or aromatic hydrocarbons. Evidently, the cation **284** is more stable than the cation **280** and, hence, the reaction of the alkene **8** with the alcohol **281** occurs under markedly milder conditions than that with the alcohol **278**. The dissimilar reaction pathways observed in the case of benzyl alcohol and benzhydrol may be due to the differences between the enthalpies of formation of the camphenyl cation, the ion **284** and the benzyl cation from the corresponding precursors; this assumption was confirmed by AM1 and PM3 calculations.⁸⁹

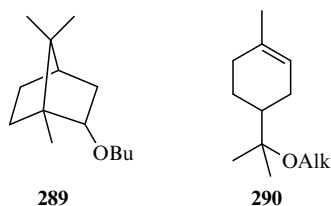
α,α -Dimethylbenzyl alcohol **285**, which is also capable of forming a stable benzyl cation, apparently does form it. This cation (**286**) is then converted into α -methylstyrene **287**; the latter is more nucleophilic than the alkene **8** present in the reaction mixture and, therefore, it reacts with the cation **286** to give 1,3,3-trimethyl-1-phenylindane (**288**).



Thus, aliphatic-aromatic alcohols, depending on their structure, can react with camphene on zeolites according to two pathways: (1) to give ethers — *O*-alkylation; (2) to give hydrocarbons with the formation of a new ring or a new linear chain — *C*-alkylation. The process yielding indane derivatives does not involve the alkene **8**.

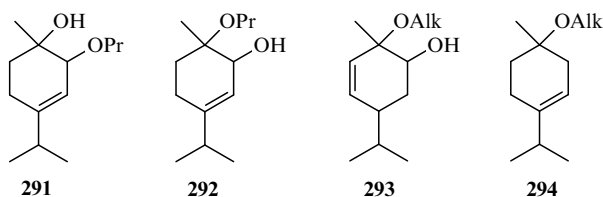
The reaction of **8** with aliphatic alcohols, for example, with methanol, on the β -zeolite also leads to ethers (**275d–277d**). The preparation of the ether **276d** from **8** and methanol in the presence of the HSZ-330HUA zeolite has also been reported.⁹⁰

This zeolite was also used to obtain ethers **289** and **290** from tricyclene **237** and butanol and from 2- and 3-carenes and alkanols, respectively.⁹⁰

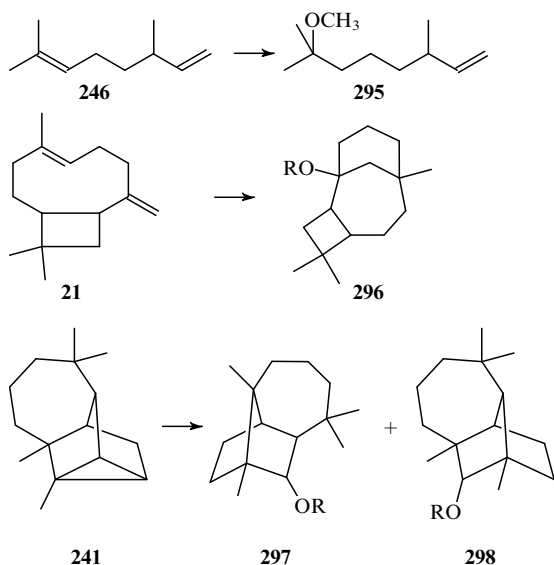


The reaction of α -terpinene **4** with propanol on the HSZ-600HOA zeolite gives rise to a mixture of compounds **291** and **292**.

When α -phellandrene reacts with C_1 – C_4 alcohols under the same conditions, compounds of type **293** are formed.⁹¹ At the same time, alkoxylation of γ -terpinene **5** on zeolites of the 300 series affords ethers **294**.⁹²



Some terpenoids undergo skeletal rearrangements during alkoxylation with C_1 – C_4 alcohols. For example, dihydromyrcene **246** is converted into ether **295** with a terminal double bond, β -caryophyllene **21** yields tricyclic product **296**, and longifolene **9** gives products **297** and **298**.⁹²



IV. Conclusion

Analysis of the data considered in this review leads to interesting conclusions. The main of them is that many concepts and regularities of the chemistry of homogeneous reactions customary for organic chemists, such as homology, isomerism, vinylogy, *etc.*, cannot be transferred directly to the reactions of polyfunctional compounds occurring on the surface of heterogeneous catalysts (mostly aluminosilicates). In fact, even the closest homologues (acrolein and α -methylacrolein), vinylogues (formaldehyde and acrolein) and isomers (α -methylacrolein and crotonaldehyde) react in different ways in this case. The functional group in the reactant also does not play a crucial role: acrolein and α -methylacrolein react with camphene to give quite different products, whereas the products obtained from acrolein and methyl vinyl ketone are similar. The reaction route is determined not only by the structure of the reagent, but also by the structure of the

substrate. For example, despite the fact that the bicyclic fragment in camphene and the benzene ring in styrene do not formally participate in the reaction with acrolein, which involves only the double bonds of these compounds, the reaction outcomes are totally dissimilar.

These speculations prompt the thought that the role of a heterogeneous catalyst does not always reduce to mere acid catalysis, although it is owing to the acid properties of the catalysts that some reactions can be conducted under milder conditions and their selectivities and the yields of products can be increased. However, the main role of a heterogeneous catalyst is to ensure a certain orientation of the molecule with simultaneous decrease in the energy barriers to many transformations, and this often sets the process on an unusual pathway.

The lack of understanding of the regularities of adsorption of even simple organic substrates on the surface of a catalyst hampers the prediction of the behaviour of complex polyfunctional compounds, such as terpenoids, under these conditions. The currently available experimental data permit only some empirical conclusions to be drawn. However, accumulation of knowledge in this interesting field of organic chemistry will certainly make it possible to generalise and classify the information and, hence, to predict with confidence the reactivities of various substrates. Finally, it should also be mentioned that, although the research in the field of reactions of terpenoids on heterogeneous catalysts is still being carried out by the 'trial and error' method, important and interesting results have already been obtained, owing to the polyfunctionality and conformational flexibility of the substrates under consideration and also owing to abnormal orientations, compared to those in homogeneous reactions, of reacting molecules on the surface of catalysts.

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Chemical approaches to the study of template biosynthesis: general problems and the study of transcription

D G Knorre, N V Kudryashova, O I Lavrik

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Abstract. The chemical approaches to the study of systems for template biosynthesis are examined. The general problems of template biosynthesis solved with the aid of these approaches and the principal results obtained as regards transcription are described. Attention is concentrated on the results obtained in the study of the interaction of RNA polymerase and its subunits with DNA and the RNA product. The approaches to the study of the active centre in RNA polymerases by the affinity modification method as well as the interaction of eukaryotic transcription factors with DNA are described. The bibliography includes 64 references.

I. Introduction

The enormous role of chemical methods in the study of proteins, nucleic acids, and their complexes, which perform the most refined functions in living organisms, including template biosynthesis systems, is well known and unquestionable. Chemical methods constitute the basis of many most important stages in the determination of the primary structures of proteins and nucleic acids. It is sufficient to mention the Edman procedure for the stepwise cleavage of peptides, the basically chemical method of Maxam–Gilbert which revolutionised the determination of the DNA nucleotide sequences, and the Sanger sequencing method based initially on the employment of chemically synthesised dideoxynucleoside-5'-triphosphates and subsequently automated by the introduction of fluorescent dyes either into terminators or primers. The development of convenient and effective methods for the chemical synthesis of polypeptides and oligonucleotides has played an inestimable role in the study of biopolymers and their functions. We shall not consider these two groups of chemical approaches, but it is understood that the primary structure of any protein and of any nucleic acid can be established and polypeptides or oligonucleotides of sufficient length (tens or several

hundreds of monomer units) may be synthesised chemically when this is needed or when it is of interest to do so.

In the present review, attention is concentrated on the use of the chemical reactions of proteins and nucleic acids to study systems of template biosynthesis. Three groups of chemical methods will be dealt with.

The first group includes methods for the chemical cleavage of polymer chains under mild conditions. Naturally, any biopolymer can be disintegrated into fragments on sufficiently severe treatment. For example, RNA may be hydrolysed to mononucleotides in an alkaline medium. However, under conditions necessary for alkaline hydrolysis the tertiary structure of RNA is disrupted. Furthermore, in the review attention is concentrated on the application of chemical approaches to the study of functionally active biopolymers, and for this purpose one has to deal with a native biopolymer whose tertiary structure is disrupted to a minimum extent. Methods of cleavage under mild conditions, which do not distort the steric organisation of biopolymers and their complexes, will therefore be described and considered. Up to now these approaches have found extensive application only in the study of nucleic acids.

The second and third groups include methods for the chemical modification of biopolymers. Chemical modification is understood as chemical reactions which do not lead to the degradation of the main polymer chain. Two principal types of chemical modification are distinguished: the group-specific and affinity modification. In the first case, use is made of a reagent capable of modifying particular types of biopolymer residues, usually amino-acid side groups or the heterocyclic bases of nucleic acids.

In the second case, a ligand capable of specific interaction with the biopolymer, for example the substrate of any kind of enzyme, is provided with a reactive group. As a result of the affinity for a particular site of the native biopolymer, the reagent is fixed on this site and the chemical reaction takes place in the vicinity of the latter.^{1,2}

Much has been hoped for of the chemical modification methods as regards the study of the structures and reactivities of biopolymers.

Thus, by studying with the aid of a group-specific reagent which of the biopolymer residues potentially capable of modification should actually be modified, it may be inferred which of them are in a position accessible to the reagent, *i.e.* which are concealed within the protein globule and which participate in the hydrogen bonding forming the secondary or tertiary structure of the nucleic acid. Furthermore, by comparing the degree of

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biopolymer modification by such a reagent with the degree of loss of biological activity, the involvement of the modified residues in the functioning of the biopolymer may be inferred.

By employing affinity reagents, the modified residue may be identified. It was assumed that this is one of the residues forming the active centre of the biopolymer or is at least in the vicinity of the active centre.

In order to investigate systems consisting of several biopolymer molecules (subunits), bifunctional chemical reagents, capable of reacting with the two functional groups of the biopolymers, may be used. This led to the possibility of obtaining information concerning the subunit areas which are at a sufficiently close distance from one another, permitting one molecule of the reagent to react with both polymeric components (to cross-link them into a single structure).

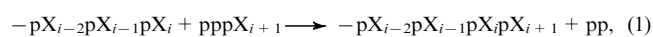
However, during the last decade, many changes have occurred in physicochemical biology which have made it necessary to correct our view on the possibilities and principal tasks of the chemical modification methods. Thus the tertiary structures of many enzymes, including those participating in template biosynthesis, have been established by X-ray diffraction. In certain cases, the structures of complexes of proteins with specific ligands or their analogues were determined, *i.e.* data were obtained concerning the disposition of the ligand (substrate) on the protein. The importance of individual aminoacid residues in the functioning of the protein can be readily established with the aid of site-specific mutagenesis — the specific replacement by genetic engineering methods of a particular aminoacid residue by any other out of the 20 residues constituting proteins. Therefore, in applying chemical approaches to the study of systems of template biosynthesis, it is necessary to take into account the current possibilities of both direct physical methods and genetic engineering.

Together with the exposition of the main data obtained with the aid of chemical methods for the study of RNA and DNA polymerases, an attempt will therefore be made to examine which principal possibilities and advantages are provided by chemical approaches in the study and practical employment of systems of template biosynthesis. However, we shall deal initially with the general problems faced by investigators in the field of template biocatalysis.

II. Certain general problems of the template biosynthesis of nucleic acids[†]

Nucleic acid polymerases possess a set of features of many other enzymes. Like any other enzymes, they act on specific substrates, which are in this case the growing polynucleotide chain and nucleoside 5'-triphosphates (henceforth abbreviated in the general case and for ribonucleotides as NTP and for deoxyribonucleotides as dNTP).

Polymerases have an active centre which catalyses the transferase reaction, the transfer of the nucleotide residue of the NTP from the pyrophosphate to the 3'-OH group of the growing polynucleotide chain. In terms of the single-letter nucleotide nomenclature, this reaction can be formulated as follows:



where X is the nucleoside, *i* the index designating the position of the nucleoside in the polynucleotide chain, and p the phosphoric acid residue.

However, there are many specific aspects characteristic either solely or predominantly of enzymes of template biosynthesis. These aspects are apparently characteristic also of the biosynthesis of proteins on ribosomes.

Firstly, the normal function of polymerases of nucleic acid requires the presence of a template with the aid of which one out of the four NTPs present in the system is selected at each step of chain lengthening. Four types of nucleic acid polymerases, differing in

the chemical nature of the template and in the substrates, are known. DNA polymerases catalyse the template biosynthesis of polydeoxyribonucleotide chains, using either DNA (DNA-dependent DNA polymerases, usually called simply DNA polymerases) or RNA (RNA-dependent DNA polymerases or reverse transcriptases) as the template. RNA polymerases synthesise polyribonucleotides using either DNA (DNA-dependent RNA polymerases or simply RNA polymerases) or RNA (RNA-dependent RNA polymerases or RNA replicases) as the template. The processes catalysed by these enzymes are referred to simply as replication, reverse transcription, transcription, and RNA replication. DNA and RNA polymerases are characteristic of all living organisms without exception, and these enzymes have already been the subject of intensive investigations, by procedures including chemical methods, in the course of many years. Vigorous studies on the reverse transcriptases present as the obligatory component of retroviruses, which include the HIV-1 virus responsible for AIDS, have been initiated in recent years.

The selection of the required monomer at each stage of the lengthening of the polynucleotide chain via reaction (1) must serve as the signal for the switching on of the catalytic centre effecting the transfer of the α -phosphate of the nucleotide residue to the 3'-OH group of the growing chain. This may be associated with the more refined adjustment of the structures of the substrates to the groups of the catalytic centre of the enzyme in response to the recognition of the correct substrate.

Secondly, at each chain lengthening stage one nucleotide base of the template, working as an information element, is involved in the selection process. The active centre of the enzyme consists of three main subsites (Fig. 1): the site accommodating the information unit of the template, ensuring the selection of the monomer (A) required at the given stage, the site in which the substrate is bound in its prereaction form (B), and the site accommodating the 3'-terminal unit of the growing chain to which the new nucleotide residue (C) is attached. In this scheme, the selection step takes place at the junction between sites A and B. If it is assumed that a certain time after the addition of the nucleotide unit the participants in the process remain in their places, the following situation is created: site C is occupied by the penultimate nucleotide residue of the lengthened chain; site A is occupied by the information element already employed; site B is occupied by the 3'-terminal

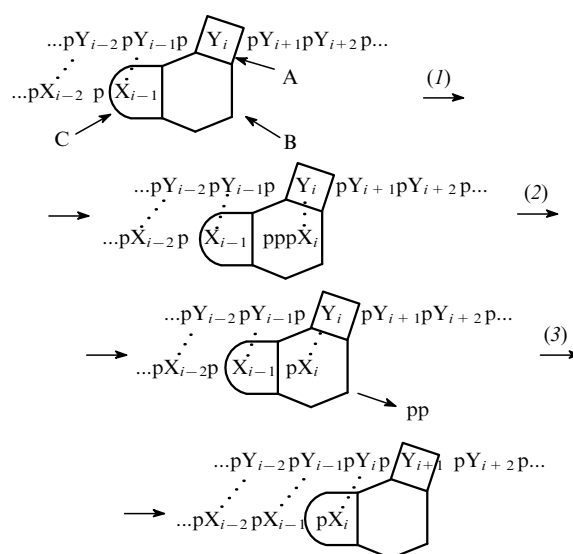


Figure 1. Processes occurring in the active centre of a template enzyme on elongation: Y is information elements of the template, X is monomer units of the growing chain; pppX_i is free monomer; A is binding section for the information element of the template, B is monomer binding section, C is binding section for the end of the growing chain. (1) Selection of the monomer; (2) formation of a chemical bond; (3) translocation.

[†] The general problems of the template biosynthesis of nucleic acids have been examined by Knorre and Myzina.³

unit of the lengthened chain. It is reasonable to assume that all three domains of the enzyme are unique. In this case, the continuation of the synthesis requires the specific displacement of the template–growing chain system relative to the enzyme by one unit — translocation. The process can occur either synchronously with the chemical reaction or can follow it.

Thirdly, the initiation of the synthesis of new polynucleotide chains begins from a definite start point. The method of specifying this start point is different for polymerases of various types. In the case of transcription, the RNA polymerase must be located, before initiation, on a particular section of the DNA template, usually outside the region where transcription should occur. This section is referred to as the promoter if it is not too far (within the limits of tens of nucleotide pairs from the start point) or as the enhancer, as is the case for eukaryotes. There is, in addition to the promoter, a centre significant for the initiation of transcription located several hundreds or even thousands of nucleotide pairs from the start point. A random collision of the enzyme with the promoter appears to be a very improbable event. There is therefore the problem of the search for the promoter (or enhancer) by the enzyme or a special auxiliary protein — the transcription factor, which subsequently assists in the correct placing of the RNA polymerase near the start point.

It is noteworthy that in all the cases investigated initiation occurs only with the aid of RNA polymerases. Not one instance of initiation with the aid of DNA polymerase is known hitherto. These enzymes are capable only of lengthening an already existing chain. The synthesis of new DNA molecules in the cells therefore begins with the synthesis by a special enzyme of a short ribooligonucleotide, which is subsequently lengthened by the DNA polymerase, apparently this time with the aid of a second active centre. In the experiment, this can be achieved by introducing into the system a short deoxyribooligonucleotide complementary to the template. This oligomer can be subsequently lengthened with the aid of DNA polymerase. Such oligonucleotides have been called primers and the RNA polymerase generating the RNA primer for the subsequent synthesis of DNA is referred to as the primase. After the synthesis of the short RNA fragment by the primase, the growing end of the chain is switched to work with the DNA polymerase. This refers to cell enzymes. For enzymes the synthesis of which is programmed by viral nucleic acids, there are alternative paths. The initiation of the synthesis of DNA with the aid of the reverse transcriptase of retroviruses is being most intensively investigated. In this case, the genome viral RNA captures the primer from the cell, the role of the primer being assumed by one of the tRNA of the host cell, the 3'-end of which is complementary to a definite section of the genome RNA (the primer binding section), whereupon the reverse transcription begins with the attachment of the dNTP residue to the 3'-terminal ribonucleotide of the primer.

All the aspects of the functioning of polymerases enumerated — the adjustment of the selected substrate with the aid of the information element to the catalytic centre, translocation, the search for start points, and the directed switching of the template — product complex from one active centre to another — are dynamic events. Although dynamic elements are present also in the functioning of other types of enzymes, one can claim confidently that the role of dynamics in the functioning of template enzymes is especially important.

The second specific feature of template biosynthesis (especially characteristic of processes in eukaryotes) is that transcription and replication occur in a highly organised multicomponent system. In the case of eukaryotes, such a system is chromatin. In both transcription and replication, several components participate directly in the biosynthesis of nucleic acids. These must be combined in a single complex to effect the process. For example, transcription precedes the formation of a complex between the template and a set of transcription factors. The processivity of replication (the occurrence of a large number of elongation stages without the dissociation of the enzyme–substrate complex) is

ensured by the presence of special clamping proteins which prevent dissociation. The knowledge of the structure of these complexes and of the dynamics of their changes during the functioning of the template system is extremely important for the understanding of the mechanism of the functioning of nucleic acid polymerases under the conditions in the living organism.

Yet another characteristic feature of template processes is that template systems must involve a template having an arbitrary primary structure. RNA polymerase must interact with an arbitrary transcribable sequence, which moves along the enzyme in the course of transcription. There are grounds for the assumption that the RNA synthesised remains for some time in contact with the enzyme. If this is so, then a certain 'exit corridor' for the transcription product should exist on the enzyme (Fig. 2, section *f*). DNA polymerase interacts with any template susceptible to replication, moving along it in such a way that only the information residue of the template and the 3'-end of the product are located in the active centre. It may be expected that a segment of the as yet nonreplicated template as well as a section of the duplex produced are in contact with the enzyme over a certain distance. The region of contact with the latter can also be referred to as the exit corridor. The problem of the determination of the region of the nonspecific contact between the enzyme, on the one hand, and the template and the polymeric product, on the other, therefore exists for template systems.

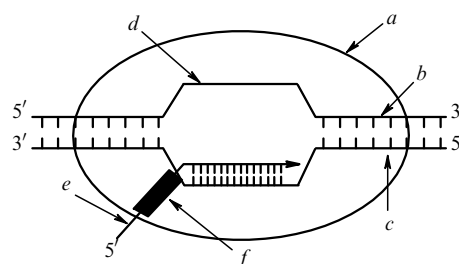


Figure 2. Schematic illustration of the interaction of the chains of the template and the product during transcription: (*a*) RNA polymerase; (*b*) nontranscribed DNA strand; (*c*) transcribed DNA strand; (*d*) temporarily unwound segment of DNA (bulge); (*e*) product RNA (transcript); (*f*) product RNA exit corridor.

By virtue of the length of nucleic acids and the presence as a rule of 'singular points' on the molecules of nucleic acids with the aid of which a definite catalytic step (initiation of transcription, onset of the repair process) should take place, the problem of the search for these singular points arises — for example, the search for the promoter by RNA polymerase, the search for the damaged point by repair enzymes, *etc.* In this connection, yet another problem of template biosynthesis is the determination of the mechanism of the search for such singular points.

III. Specific chemical approaches used in the study of nucleic acid polymerases

The majority of the problems arising in the study of template biosynthesis required the knowledge of the region of contact between nucleic acid and other components of the system, in the first place proteins. The region of contact is to a large extent protected against the influence of external factors, in particular enzymes and chemical reagents. When any kind of agent acts on the free biopolymer and on the polymer involved in a specific complex, it is in principle always possible to compare regions modified in the presence or absence of other components of the system and hence to determine which region is covered by these components. However, in the current state of experimental methods such a problem can be readily solved only for nucleic acids. The nucleic acid may be labelled at one of its ends. If it is treated by an endonuclease or a reagent cleaving the polynucleo-

tide chain at the modification point and the process is carried out to an extent such that on average there is one break for each chain, then the mixture obtained after separation by gel electrophoresis gives rise to a series of bands corresponding to cleavage products of different lengths (counting from the labelled end). When highly radioactive phosphorus or an intense fluorescent label is used, only fragments which have retained the labelled end are determined on the gel. If the nucleic acid has no tertiary structure, a series of bands corresponding to all the imaginable break points within the limits of the resolution of the electrophoresis are obtained. On the other hand, if during treatment the nucleic acid forms a complex with a protein or several proteins, then, within the limits of the region of contact, no cleavage occurs or at least it is not very pronounced. In this case, a 'white' spot, *i.e.* a region without radioactivity or a nonfluorescent region, appears on a series of bands. This spot is the imprint of the segment bound to the nucleic acid and is referred to as the footprint. Naturally, the effects of reagents used should not influence the stability of the complex investigated.

In footprinting, it is desirable that the specificity of the cleavage reaction in relation to heterocycles should be low. It is noteworthy that, together with chemical reagents, enzymes hydrolysing nucleic acids are frequently employed for footprinting. For this purpose, use is most often made of DNase I, which catalyses the cleavage of the inner phosphodiester bonds, including those in double-stranded DNA, leading ultimately to the formation of a set of relatively short oligonucleotides, as well as exonuclease III from *E. coli*, which catalyses the stepwise splitting off of the 5'-nucleotides from the 3'-ends of both strands of the double-stranded DNA. However, the resolution of the methods based on enzymic cleavage is restricted by the size of the enzyme (the larger the enzyme, the smaller the resolution), which in the case of DNA polymerase I is ~ 4 nm in diameter.⁴

A significantly better resolution is achieved when chemical reagents of small size are employed. The free radical $\text{HO}^\bullet$, generated in the $\text{Fe}(\text{EDTA})^{2-}/\text{H}_2\text{O}_2$ system, has recently come to be widely used for the cleavage of DNA.⁵ A specific feature of this method is that the reactions proceed via deoxyribose, which makes the method more specific in relation to the sequence of nucleotides. Footprinting with the aid of KMnO_4 is also used to investigate polymerases.⁶

In principle, it is possible to obtain a similar footprint of the protein molecule interacting with nucleic acid. Until recently, such studies were held back by the lack of effective methods for the determination of the points of modification of the protein, which made this problem extremely difficult. Very recently, a study has been published⁷ in which a highly radioactive label was introduced into the transcription factor TFIIB by attachment to the C-end of the pentapeptide 'tail' — arginylarginylalanylserylvaline, which is the target for phosphorylation with the aid of heart muscle protein kinase. This made it possible to introduce the [^{32}P] phosphate residue at the OH group of serine and then to carry out single-impact hydrolysis of the protein with the aid of weakly specific proteases with subsequent electrophoretic separation of the set of peptides obtained. As in the footprinting of nucleic acids, only peptides containing the C-terminal fragment and differing in their lengths appeared on the radioautograph. Comparison of the set of peptides obtained from the initial transcription factor and its complex with yet another factor TAF made it possible to identify the region protected by this factor against proteolytic cleavage by TFIIB.⁷

The existence of the elongation stage leads to interesting possibilities both in the methods whereby affinity modification can be carried out and in the design of reagents for affinity modification. Among the modification procedures, the method which has been called highly specific or competent labelling is especially interesting.⁸ Nucleotides and their derivatives are in many cases capable of interacting not only with the active centre of the enzyme but also with a set of other regions on the surface of the protein. Cases are known where a large number of molecules

of a reactive nucleotide derivative are bound to the enzyme molecule and such interaction is not always accompanied by the loss of enzyme activity. For example, the photoaffinity modification of phenylalanyl-tRNA synthetase from *E. coli* by ATP γ -*p*-azidoanilide can lead to the addition of 20 molecules of the ATP analogue without loss of enzyme activity.⁹ In template biosynthesis, there is a possibility of the situation where the addition of a nucleotide to a protein does not prevent its participation in the elongation process. In this case by carrying out in the first stage of the experiment the modification by a nonlabelled reagent, designed as an affinity reagent, and then adding the next NTP carrying a radioactive label, for example α - ^{32}P , it is possible to discriminate the modification point in the region of the active centre, because only the residue of the reagent attached covalently in this region undergoes elongation and contains the radioactive label. It must be emphasised that not all the residues of the affinity reagent attached to the enzyme in the region of the active centre are detected by this method because, if the modification involved the residue participating in the catalytic step, elongation cannot occur owing to the loss of catalytic activity. However, it is clear that no residues bound outside the active centre of the enzyme, even at functionally significant points, can be detected.

In the template biosynthesis of nucleic acids, the participants in the process are the template nucleic acid, the newly synthesised nucleic acid chain, and the corresponding NTP. The first two participants are polymeric molecules. The corresponding affinity reagents may be generated by synthesising the corresponding oligonucleotide fragments modelling these polymers, or by the modification of the polymers themselves. However, it is possible to introduce chemically reactive groups also during the elongation process. Derivatives of nucleoside 5'-triphosphates carrying reactive groups are used as substrates for such purposes. An example of a substrate of this kind for RNA polymerases is 5-(4-azidophenacylthio)-CTP.¹⁰ In this case, the elongation product contains a reactive group template and is already an affinity reagent in relation to the template enzyme which was used in its synthesis. The substrate which participates in the elongation step but, being incorporated in the 3'-end of the chain, cannot combine with the next nucleotide unit is optimal. It is also possible to use reactive derivatives of terminators, for example dideoxynucleoside 5'-triphosphate in the biosynthesis of DNA. In this case, the reactive group is automatically fixed in the region of the active centre of the enzyme.

As already noted, it has been hoped that affinity modification is a method which will make it possible to determine the amino-acid residues in the active centre of the enzyme and in its vicinity. However, for this purpose it was necessary to know how to locate the modified residue on the polypeptide chain. The most direct approach consists in the cleavage of the modified protein at specific points, the identification in the set of peptides obtained that which contains the modified residue, and the analysis of this peptide by stepwise cleavage with the aid of the Edman method. The appearance in the course of this procedure of an unusual derivative or the arrest of cleavage at a particular unit indicates that this is the point where modification has occurred. The nature of the modification may be inferred provided that the product of the interaction of the modified residue with the reagent employed is known (from independent experiments).

In a number of instances, it is possible to apply indirect procedures whereby one can deduce the modification point with a particular degree of reliability. Such an approach has been proposed and widely developed in the studies of Grachev and coworkers⁸ in relation to the location of the modified lysine and histidine residues in RNA polymerase by phosphorylating reagents. The properties of the phosphoramides formed on phosphorylation of the aliphatic ϵ -amino-group of lysine and of the imidazole ring of histidine differ quite sharply. Both phosphoramides are labile in an acid medium, but the kinetic characteristics of the hydrolysis are different. By measuring the rate of elimination of the attached label (demodification), it is possible to

compare the kinetic constants obtained with those measured for model compounds.[‡] ATP γ -*N*-methylamide and ATP γ -imidazolidine have been used as such compounds. The rate constants for their cleavage at pH 4.9 are 0.014 min^{-1} at 50°C for the amide and 0.016 min^{-1} at 20°C for the imidazolidine, *i.e.* they differ quite sharply. After the determination of the peptide in which the modified residue is located, it is possible to determine from the primary structure of this peptide how many aminoacid residues are present in it and at what positions. If a residue of this kind, for example a histidine residue, is the only one in this peptide, then the location of the modification point is unambiguous. When the modified protein is cleaved into fragments and when particular procedures are used to separate the mixture of peptides, one must naturally bear in mind the stability of the modification product. For example, it is clear that in the case examined one cannot use proteases acting in an acid medium for the cleavage of the protein.

The use of photoaffinity modification by bromodeoxyuridine (brdU) residues may be quoted as yet another approach. Bromouracil is known to react photochemically with cysteine, tyrosine, phenylalanine, and histidine residues.¹¹ By employing this property, Skiba *et al.*¹² investigated the modification of the *E. coli* RNA polymerase by the decanucleotide $T_3\text{brdUT}_4$ labelled with ^{32}P . Analysis of the peptides obtained by successive cleavage by bromocyanogen at the methionine residue and by trypsin hydrolysis at the lysine and arginine residues showed that the label is contained in the 721–731 peptide of the β -subunit and in the 984–990 peptide of the β' -subunit. Since each contains one aromatic aminoacid residue, the authors believe that the modification points are Tyr-726 and Phe-988 respectively.¹²

The above example demonstrates how important it is to have information about the chemical nature of the products of the modification of the aminoacid residues. Unfortunately, the modification products have been at present quite inadequately investigated for the most promising approach on the photoinduced modification, in particular for the widely employed method based on direct photocross-links between nucleic acids or nucleotides and the protein.

IV. Principal stages of transcription. The subunit structure of RNA polymerases §

So far, the main object of the detailed study of the mechanism of the functioning of RNA polymerases has remained the enzyme isolated from *E. coli*. From this example, it is easier to elucidate what can be obtained and what may be expected in the future from chemical approaches to the study of transcription. A few words must therefore be said about the enzyme itself and about the phenomenology of its functioning.

The main enzyme (core) consists of three types of subunits — α , β , and β' . The first of these is present in the form of two copies, so that the subunit structure of the enzyme is formulated as $\alpha_2\beta\beta'$. In the transcription initiation stage, the regulatory σ -subunit also enters into the composition of the enzyme, as a result of which the whole enzyme (the holoenzyme) $\alpha_2\beta\beta'\sigma$ functions. Only then is the correct complex between the enzyme and DNA formed in the region of the promoter, which in fact determines the point of the onset of transcription.

It is appropriate to mention that the numerals assigned to DNA nucleotide pairs in transcription are arranged in an increasing sequence on moving downwards, *i.e.* in the direction of motion of the enzyme during transcription, the numeral +1 being assigned to the pair coding for the first nucleotide of the transcript. In the nontranscribable section, located above the transcribable section, including the arrangement in the promoter, the numbers

are negative and the numeral 0 is absent. According to the views of Yager and Hippel,¹⁴ the transcription in prokaryotes takes place in six stages:

(1) The interaction of the enzyme with DNA is initially as a rule nonspecific but terminates with formation of an enzyme–promoter complex.

(2) Fusion of the template DNA in the region of contact between the promoter and the enzyme with formation of a locally unwound region (bulge) on the double-stranded DNA, which makes possible retranscription with the aid of the active centre of the enzyme located on the transcribable information strand (in the form of a ribonucleotide sequence).

(3) Abortive initiation, which begins with the reaction of two ribonucleoside 5'-triphosphates (NTP) selected by the DNA template,



and continues in accordance with Eqn (1) until ~ 10 elongation steps have been completed, after which the σ -subunit is split off from the complex and the latter is markedly stabilised [up to this moment, the possibility of the dissociation of the complex with ejection of a short (abortive) product, an oligonucleotide, remains].

(4) Elongation occurring in the stable complex with migration of the enzyme and the bulge along the DNA; within the limits of the bulge the 3'-terminal fragment of the newly synthesised DNA forms a duplex with the transcribable DNA strand (see Fig. 2).

(5) Encounter between the enzyme and the nucleotide sequence in the transcribable DNA, which is potentially capable of promoting termination.

(6) Decomposition of the transcription complex with liberation of the transcription product.

Naturally the active centre moves along the strand being transcribed and a hybrid duplex comprising the fragment of the strand being transcribed and the RNA product is formed on the region between the start of the bulge and the active centre. At a certain instant, the RNA product begins to separate from the template, whereupon the latter is rejoined to the nontranscribed strand. On the other hand, the DNA strands continue to move apart ahead of the active centre migrating along the strand being transcribed.

In recent years, studies by chemical methods of eukaryotic RNA polymerases have begun to be published. These enzymes have a significantly more complex structure than the enzyme from *E. coli*. They consist of approximately ten different subunits. Furthermore, three different RNA polymerases, usually designated as RNA polymerases I, II, and III, function within the cores. For yeast the corresponding enzymes are designated by the Latin letters A, B, and C. These enzymes are respectively responsible for the transcription of the genes of the ribosomal RNA, the genes of information RNA, and the genes coding for various small RNA, including transport and ribosomal 5S RNA. The subunit composition of certain, most intensively investigated enzymes is presented in Table 1. An important distinctive feature of eukaryotic enzymes is the need for the involvement of special transcription factors in the transcription initiation process. According to the available data, the functionally significant interaction of all three RNA polymerases with DNA begins with the formation of a complex between DNA and the set of transcription factors specific to each of the three polymerases.

Thus the following problems are solved (or can be solved) with the aid of chemical methods. The first is the establishment of the nature of the subunits interacting with DNA and the study of the dynamics of the primary interaction of the enzyme with DNA. These problems can be solved by the direct photocross-linking method. The second is the establishment of the region of DNA interacting with the enzyme at different transcription stages, which may be achieved with the aid of footprinting. The third is the determination of the size and position relative to the enzyme of the 'bulge' migrating along DNA, which can be achieved by identifying the DNA residues not involved in the Watson–Crick

‡ If the phosphorylation occurred at serine, threonine, or tyrosine residues, the modification product would be stable in the pH range used for demodification. Thus the knowledge of the chemical nature of the modified residue makes it significantly easier to locate it.

§ For the principal concepts, see Alberts *et al.*¹³

Table 1. The subunit composition of eukaryotic RNA polymerases (in kDa).

Yeast			Wheat seedlings	Calf thymus		Human HeLa cells		Drosophila	
A	B	C	I	I	II	I	II	I	II
190	220	160	180		210	197	240	195	175
	185				180		214		
135	150	128	140– –150		145	140	180	125	135
		82				126			
49	53			51		52		48	
43	44.5			44	44			41	
40		40			36			38	
34.5	32	31	30						
27	27	27		25	25			25	
23	23	23			20				
19		19			18			18.5	
	16.5				16.5	16			
					15, 12, 11.5				

interactions. The fourth is the identification of the subunits participating in the interaction with the DNA strands in the region of the bulge, with the newly synthesised RNA before and after its separation from the template DNA (establishment of the exit corridor), and with the substrates (NTP). The last range of problems may be solved with the aid of the affinity labelling of the components by the corresponding reactive analogues, including the use of competent labelling, or by direct photocross-linking on UV irradiation. For adequately stable products, it becomes possible to establish the positions of the interacting aminoacid residues by identifying the modified aminoacids. In this case, one obtains information about the individual elements of the active centre of the enzyme. For eukaryotic enzymes, the study of the region of DNA interacting with the transcription factors and also the interaction of the latter with the enzyme itself are added to these tasks. We shall examine consecutively the principal results obtained by applying chemical approaches to the solution of these problems.

V. Interaction of RNA polymerase and its subunits with DNA

The first experiments designed to investigate the interaction of RNA polymerase with DNA were carried out by means of the chemical method easiest to use — the method of direct photocross-links. A mixture of DNA and the enzyme irradiated with UV light (usually at $\lambda = 254$ nm) is treated with the corresponding nucleases, after which only small fragments of the attached DNA are retained in the form bound to the enzyme. The enzyme subunits are separated by gel electrophoresis and the subunits bound covalently to DNA on irradiation are found from the positions of the radioactively labelled bands. It is also possible to treat the irradiated mixture with restriction enzymes, which cleave DNA at strictly defined sections, to precipitate with the aid of antibodies to RNA polymerase the fragments which contain the covalently bound enzyme, to remove the enzyme from the precipitated fragments by treatment with the corresponding proteinase, and, having separated them by gel electrophoresis, to find from the positions of the bands which of the fragments and in what amount were cross-linked with RNA polymerase on irradiation.

The results of the first study of this kind are presented in the paper of Hillel and Wu.¹⁵ It was noted that, when an excess of the enzyme is mixed with ³H-labelled DNA of T7 phage and on subsequent UV irradiation of the mixture, the main part of the enzyme is bound outside the promoters, *i.e.* nonspecifically. If an excess of unlabelled DNA is added to the mixture before irradiation, then the complexes between labelled DNA and the pro-

moters are retained for a fairly long time and the labelled DNA in the nonspecific complexes is replaced by the unlabelled DNA, so that on UV irradiation the radioactivity is retained only in the specific complexes. It was established in this way that three subunits (β , β' , and σ) participate in the nonspecific interaction, while only β and σ are involved in the formation of specific complexes. In both cases, there is no interaction with the subunit α .

It has been shown using DNA in which thymine had been substituted by bromouracil, affording more stable cross-linking products,¹⁶ that the third heterocycle in the upward direction from the start point (the -3 pair) participates in one of the cross-links in the σ -subunit, while the $+3$ pair participates in one of the cross-links in the β -subunit.

Similar results, which agree in principle with those presented on the basis of photocross-links, have been obtained on cross-linking the enzyme with DNA by means of formaldehyde.¹⁷ The procedure developed by Mirzabekov¹⁷ for the study of the interaction of DNA with histones in chromatin was used for these purposes. It is based on the elimination of purines from DNA to a slight extent (the purine heterocycles are split off from certain nucleotide residues with formation of the open-chain form of deoxyribose). The aldehyde groups of such DNA can interact with the ϵ -amino-groups of the lysine residues in close proximity with formation of Schiff bases, which are readily converted into stable alkylamines by treatment with sodium tetrahydroborate. The most detailed picture of the cross-linking of RNA polymerase with the promoter section of lac UV5 has been obtained¹⁸ by this method.

The results of the modification of *E. coli* RNA polymerase by the alkylating derivative of the oligonucleotide carrying at the 5'-terminal phosphate the 4-[*N*-methyl-*N*-(2-chloroethyl)amino] benzylamine residue and having a sequence corresponding to the fragment from -13 to -2 of the nontranscribed DNA strand containing the *spc* promoter have also been described. It has been established that the oligonucleotide itself has a high affinity for the enzyme, which may be evidence in support of the mechanism involving the unwinding of the double-stranded DNA in the region of the promoter as a result of the preferential binding of the nontranscribed strand and hence the liberation of the strand being transcribed. The alkylating derivative of this oligonucleotide modifies the σ -subunit. The phenomenon involving the effective binding of the octaribonucleotide, complementary to the section from -13 to -6 of the nontranscribed strand, to the enzyme, which has not so far found a satisfactory explanation, is also described in the above study; the alkylating derivative of the octaribonucleotide then modifies the β, β' -subunits.¹⁹

The dynamics of the cross-linking of the enzyme with DNA has been investigated by means of a special apparatus for rapid mixing and subsequent irradiation after a specific time interval by a powerful short (10 μ s) UV light pulse.²⁰ The distribution of the attached enzyme between eight different sections of DNA, obtained as a result of the highly specific fragmentation of DNA with the aid of the Kpn I and Mbo I restriction enzymes, was analysed for this purpose. It was found that in such cleavage the three main promoters of the T7 phage DNA are located in one fragment. During the first tens of milliseconds, the distribution was close to statistical, *i.e.* the amount of the RNA polymerase bound to the fragment was correlated satisfactorily with the size of the fragment. The redistribution of the enzyme between the fragments with its gradual accumulation in the fragment containing the promoter then took place gradually. This made it possible to determine the rate constant for the formation of primary nonspecific complexes and the rate constant for the migration of DNA in the direction of the promoter. The nature of this migration agrees with the mechanism of migration by means of one-dimensional diffusion along DNA.

The region of contact between the *E. coli* RNA polymerase and DNA has been repeatedly investigated with the aid of footprinting. Complexes formed with the promoter in the absence of transcription and in the course of the latter were investigated. In the first case, it was possible to detect and characterise three states

of the complex — closed, intermediate, and open. The best results were obtained when OH radicals were used.²¹ In the closed complex, formed at 4 °C, the region protected by the enzyme against the action of radicals is that between -4 and -53 and the transcribed and nontranscribed strands are alternately protected with the periodicity corresponding to the helical structure of the DNA. This fact shows that only one side of DNA comes into contact with the enzyme in this region. On formation of the intermediate complex (20 °C), the turns of the DNA helix are fully protected and full protection of the nontranscribed strand along the section from -10 to +21 and of the transcribed strand along the section from -13 to +18 is observed. It had been proposed earlier²² that this section be referred to as the fusion domain, whereas the region of the incomplete contact located above it should be called the recognition domain. It must be emphasised that the fusion domain does not coincide with the fused region of DNA, namely with the size of the bulge which enters into the composition of the domain, *i.e.* is significantly smaller. The part of DNA in the fusion domain, adjoining the bulge, is still (to the right) or already (to the left) in the double-stranded form. Finally, at 37 °C, whereupon the open transcription-active complex is formed, the region of contact with the nontranscribed strand is retained while a section from -7 to +2 accessible to modification arises on the strand being transcribed.

VI. Investigation of the segment of DNA unwound in the complex with RNA polymerase (the bulge)

In the study of transcription with the aid of footprinting, it is possible to detect the migration of the edges of the bulge. Thus, in the transcription the promoter lac UV5 (the first transcribed nucleotides of which form the sequence TTAACA...) in the complex with the enzyme or with the enzyme and the primer ApA simulating the first two transcription steps, the residue C in the +5 position is not alkylated by dimethyl sulfate, whereas after the addition of dTTP, which elongates the substrate by a further two units, the same residue C becomes accessible to alkylation.²³

Further investigations required the formation of a series of transcription complexes with different lengths of the transcripts. This was achieved by employing nucleotide sequences in the transcribed part of DNA favourable for this purpose. For example, the transcription has been carried out²² from the fragment of T7 DNA with the sequence (3')T(+1)AGCTCTCC...CTGTGCCGCTTA...(5') on the strand being transcribed. When the transcription is performed using the trinucleotide AUC as the primer and ATP and GTP as the substrates, the synthesis proceeds as far as the eleventh unit, since, owing to the absence of CTP from the mixture, the next step cannot be carried out. Similarly, by carrying out the transcription in the presence of CTP, ATP, and GTP, it is possible to obtain a transcription complex in which the length of the transcript is 20, because in the absence of UTP the 21st step of the synthesis cannot occur. By altering the nucleotide sequences in DNA as a result of the introduction of mutations, it is possible to obtain transcription complexes with most diverse lengths of the newly synthesised RNA. It has been established²² with the aid of footprinting by OH radicals that, when the transcript reaches a length of 11 units, the disruption of the contact between the enzyme and the recognition domain without change in the size of the fusion domain is observed. However, a further increase in the length of the transcript leads to a decrease in the fusion domain from ~30 units to 23 units. The disruption of the contacts between the enzyme and the recognition domain after the attainment of a length of 11 units by the transcript has also been recorded by means of footprinting with the aid of the Cu²⁺ - 1,10-phenanthroline system.²⁴

A more universal procedure is based on the immobilisation of RNA polymerase on a carrier.²⁵ By employing stepwise elongation (by omitting at each stage one of the four substrates), it was possible to obtain transcription complexes with different lengths of the transcript. The length of the transcript for each such

complex yields the position of the catalytic centre of the enzyme and footprinting (in the above study, exonuclease III was employed) yields the lower point of the contact between DNA and the enzyme. Systematic measurements of the distance between these two points showed that the transcription proceeds mainly continuously, *i.e.*, for each step of the migration of the enzyme active centre, the boundary of the region of the DNA - enzyme interaction undergoes unit migration. However, in certain cases it was found that the migration of the active centre of the enzyme itself does not lead to the migration of the enzyme relative to the template and after several such steps the enzyme, as it were, executes a jump over several pairs of template nucleotides.

The migration of the enzyme in jumps has been detected also in a study²⁶ involving the application of a more refined chemical technique. In this investigation, a series of transcription complexes were obtained with the length of the transcript from 11 to 20 nucleotides. These complexes were obtained by transcription on a DNA fragment containing the promoter and the sequence of the first 20 transcribed nucleotides (3')d(TAGCTCTCCCTGTG...CCGCTT...)(5'). In order to obtain the set of complexes, the transcription was initiated with the aid of the ribonucleotide pAUC using GTP and ATP as the substrates. This system yielded a complex with a transcript length of 11 units (complex 11). After its isolation by means of gel filtration and by adding CTP, complex 12 was obtained, while the addition of CTP and ATP afforded complex 14. Complex 14 was converted into complex 16 in the presence of GTP, into complex 18 in the presence of CTP + GTP, and into complex 20 in the presence of CTP + GTP + ATP. The position of the uncoiled section of DNA (the bulge) was determined by means of three reagents, each of which was specific to one type of heterocycle: thymine, adenine, and cytosine were determined with the aid of OsO₄, diethyl pyrocarbonate, and dimethyl sulfate followed by treatment with hydrazine respectively. In combination with footprinting by OH radicals, these investigations showed that, up to and including complex 18, the double helix is uncoiled ahead of the RNA polymerase and the position of the upper contact between DNA and the enzyme does not change. After the attainment of a length of 20 units by the transcript, a jump occurs and the helix is closed, passing to the double-stranded state.

The change in the size of the region of contact between the template and RNA has been recorded for transcription complexes with RNA polymerase II from calf thymus with transcripts having lengths corresponding to 135, 138, and 143 nucleotides. Footprinting with the aid of DNase I showed that the dimensions of the sections protected against hydrolysis correspond respectively to 48, 55, and 51 pairs of nucleotides.²⁷

VII. The study of the RNA exit corridor

In order to trace the migration path of the 5'-end of the transcript formed, two principal approaches were employed. One of them is based on the introduction of a reactive group into the initiating substrate or primer. The first experiments of this kind were described in studies^{28, 29} where ATP γ -*p*-azidoanilide was used as one of the substrates. The latter may serve for both initiation and elongation. Naturally the photoreactive section of γ -*p*-azidoanilide is retained only at the 5'-end of the transcript. Photomodification was detected only in the β - and σ -subunits. A more detailed study of the transcript by means of this procedure has been carried out in a study³⁰ where transcription by the *E. coli* RNA polymerase was carried out on a poly[d(A-T)] template using labelled [α -³²P] ATP and a primer containing the photoreactive label *p*-N₃C₆H₄C(O)CH₂SP(O)(O⁻)AdoPUrd. After the transcription, the transcription complex was irradiated, the labelled subunits were separated from one another, were separated by dialysis from the substrates, and were treated with PheHgOAc in order to split off the label from the transcript. The transcripts were separated by electrophoresis and were radioautographed. This made it possible to determine the amount of transcript of a

particular length bound to each subunit. It was found that transcripts with lengths of 6–8 units modify DNA preferentially, those with a length of 9–12 units modify the σ -subunit, and those with a length of 13–19 units modify the β/β' -subunit.³¹

The second procedure is based on the hypothesis that the newly synthesised template RNA within the limits of the template DNA bulge is in the form of a duplex with the DNA strand being transcribed. In this case, it can be modelled by an oligonucleotide complementary to several residues of the open part of the strand being transcribed and carrying a reactive group at the 5'-end. This was done on the A2 section of the T7 phage DNA promoter which, forming part of a complex with *E. coli* RNA polymerase, forms the open section (3')d(ATGTTAGCGA) on the strand being transcribed, the first seven residues referring to the non-transcribed region (i.e. corresponding to numbers from –7 to –1), while the dC residue is the first transcribed nucleotide.

A series of derivatives of oligonucleotides complementary to the open section and having the general structure R(pdN)_npTprC with a 3'-terminal dinucleotide complementary to the fragment A(–2)G(–1) (the first group of reagents) and R(pdN)_npdGprC with the terminal dinucleotide complementary to the fragment C(+1)G(+2) (the second group of reagent), where R is the reactive group, were prepared. The group R contained either a benzaldehyde residue (see below) or a fragment of an aromatic 2-chloroethylamine derivative capable of alkylating the nucleophilic centres of proteins and nucleic acids, or a phosphate activating group, for example *N*-methylimidazole. After the affinity modification with the aid of the first group of reagents, [α -³²P]GTP was added to the reaction mixture and competent labelling was carried out, i.e. the label was introduced into the oligonucleotide bound covalently to the enzyme. In the case of the second group of reagents, [α -³²P]UTP was added in order to carry out the competent labelling. Next a study was made of the distribution of the radioactivity among the subunits and the presence of the histidine and lysine residue modification was detected (with the aid of the criteria described above, based on the kinetics of the demodification of the phosphorylation products). In the case of alkylating reagents, the modification of DNA was also observed. The distribution and nature of the labelled aminoacid residues differed significantly for reagents with different lengths of the oligonucleotide component, i.e. with different distances between the chemically reactive group and the G·C(+1) pair. Fig. 3 presents the results of the determination of the 'exit corridor' obtained with the aid of the first group of reagents.³² The data obtained using the second group of reagents³³ agree qualitatively with those presented in Fig. 4 for reagents of the first group. However, there are also distinct differences. For example, the σ -subunit is modified by reagents of the first group at both lysine and histidine residues and the group R cannot be attached closer than to the residue forming the –7 pair. On the other hand, when reagents of the second group were employed, the modification of the histidine residues in the σ -subunit was already observed in the modification by the hexanucleotide ($n = 4$).

The determination of the RNA exit corridor for human RNA polymerase II (HeLa cells), based on the photoaffinity modification of the enzyme with the aid of the transcript into which 4-thiouridine monophosphate (s⁴UMP) residues were introduced during transcription, has also been described. The length of the transcripts was regulated by introducing 3'-CH₃O-GTP as the terminator. Mainly large subunits with masses of 240 and 140 kDa were modified.³⁴ It was found that the length of the transcript must correspond to at least 16 nucleotide residues for sufficiently effective modification. This makes it possible to infer the distances between the active centre and the start of the exit of the transcript from the duplex formed by the transcribed DNA strand and the transcription product.

This procedure has also been used to identify the subunits in contact with the transcript, formed in the isolated nucleoli, in which ribosomal RNA genes are transcribed with the aid of RNA polymerase. For this purpose, s⁴UTP and labelled CTP were

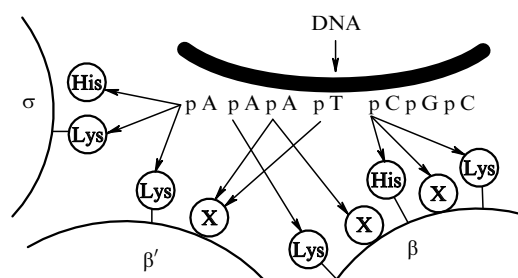


Figure 3. Topography of the product RNA exit corridor obtained by labelling the transcription complex of the *E. coli* RNA polymerase by reagents containing aldehyde and alkylating groups, and by phosphorylating derivatives of oligoribonucleotides. The arrows indicate the interactions of the reactive groups of the reagents with the aminoacid residues of the protein — Lys, His, and X (X is an aminoacid residue other than lysine and histidine).

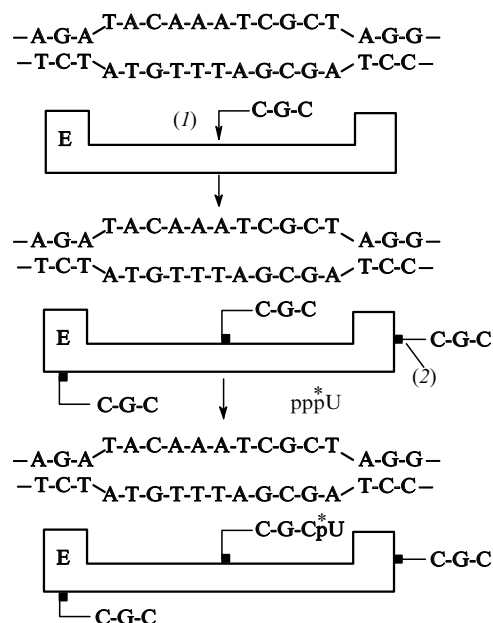


Figure 4. Schematic illustration of the highly selective affinity labelling of RNA polymerase. (1) Phosphorylating residue; (2) site of addition of the phosphorylating residue to the protein.

introduced into the nucleoli of the HeLa cells and UV-irradiation was carried out for a time. Analysis of the radioactivity associated with the RNA polymerase I isolated from the irradiated nucleoli showed that subunits with masses of 200 and 120 kDa are modified in the first place. With increase in the size of the transcript, the fraction of the transcript bound covalently to the subunit with a mass of 52 kDa also increases.³⁵

The same system has been used to locate RNA polymerase II in the nucleus. It was established that, after the irradiation of the nuclei in which transcription with participation of s⁴UTP and labelled CTP took place, the enzyme molecules are not bound to the nuclear template but move along loops formed by chromosomal DNA.³⁶

VIII. Approaches to the study of the active centres of RNA polymerases by the affinity modification method

Most of the information about the aminoacid residues of the enzyme participating in the formation of the active centre or adjoining it has been obtained by the highly selective labelling method described above. The initiating region of RNA polymerases from various sources such as the enzyme produced by the T7

phage,³⁷ three yeast RNA polymerases,³⁸ and the RNA polymerase II from human placenta³⁹ and from wheat seedlings⁴⁰ has been investigated by this method. Derivatives of the initiating purine nucleotide containing benzaldehyde at the 5'-end and forming a Schiff base with the ϵ -aminogroup of lysine were used as the affinity reagent in the above investigations. The Schiff base was reduced with tetrahydroborate to an alkylamine, after which elongation was carried out with the aid of the labelled [α -³²P]NTP. Adenosine 5'-trimetaphosphate was used to modify the region of the initiation of transcription. In the case of eukaryotic enzymes, the second subunit in terms of size was labelled. In the case of the T7 RNA polymerase, the 631 lysine residue was modified.⁴¹ In the *E. coli* RNA polymerase, the modification points were the 1065 lysine residue and the 1237 histidine residue of the β -subunit.⁴² In the yeast RNA polymerase II, the 979 and 987 lysine residues were modified.⁴³

By virtue of its high selectivity, the competent labelling method may be applied also in cell extracts. Although this has been done on RNA replicase (which we do not consider because of the scantiness of the available data),⁴⁴ we thought it useful to present an example of the determination of the functions of two nonstructural proteins of the tick encephalitis virus, because it demonstrates the possibilities of the use of the above approach in complex supermolecular systems. The UUC(3') sequence is present at the 3'-end of the plus-chain of the viral RNA, from which replication should begin in order to form the double-stranded replicated RNA. The reactive analogue from which replication may begin should be a derivative of GMP. In competent labelling, elongation should be achieved with the aid of [α -³²P]ATP. When these components were introduced into the cell extract from pig embryo kidneys infected with the virus, the radioactive label was detected in a protein with a molecular mass of 69 kDa 8 h after infection, which, judging from the spectra of the viral RNA, corresponds to the nonstructural (*i.e.* not entering into the composition of the mature virus) NS3 protein. In the extract obtained from the cells isolated 45 h after the start of infection and subjected to the same treatment, the label was present in another nonstructural protein (NS5) with a molecular mass of ~ 100 kDa. In conformity with the logic of the events characteristic of RNA-containing viruses, one may assume that the NS3 protein participates in the replication of double-stranded RNA, required for the conversion of the viral RNA into the double-stranded form while NS5 participates in the replication of the double-stranded RNA needed for the accumulation of new plus-chains entering into the composition of new viral particles.

5-Azido-UTP⁴⁵ and 8-azido-ATP have also been proposed for the direct modification of NTP-binding centres.⁴⁶ The first proved to be the substrate of the enzyme from *E. coli* with $K_m \sim 80$ μ M. Photoirradiation of the enzyme in the presence of this reagent leads to approximately the same incorporation of the label into the β -, β' -, and σ -subunits, the presence of DNA not influencing the distribution of the label between the subunits. 8-Azido-ATP is a poor substrate for this enzyme, but it inhibits the enzyme competitively (in relation to ATP). Photoaffinity modification leads mainly to the modification of the β' - and σ -subunits. When the analogue is incorporated in the 3'-terminal position in the transcript and on subsequent irradiation, the β' -subunit is modified within the limits of the 932–1020 peptide.⁴⁷ 8-Azido-ATP has also been used for the photoaffinity modification of the RNA polymerase coded for by the T7 phage⁴⁸ and of the RNA polymerase II from calf thymus.⁴⁸ Peptides containing the attached photolabel were isolated in these two investigations.

Affinity modification makes it possible to detect the migration of the substrate within the limits of one enzyme molecule or between subunits. As an example, one may quote a study⁵⁰ in which the transformation of the transcription-active complex formed by the enzyme from *E. coli* into an inactive complex was observed when transcription ceased as a result of the lack of substrate for the next elongation step. This transformation occurs when the system is incubated for several tens of minutes at 37 °C and is irreversible, *i.e.* the addition of substrate no longer leads to

continuation of transcription. The complex was obtained by stepwise elongation on the immobilised enzyme²⁵ and it contained the photoreactive 4-thio-UMP residue at the 3'-end. The complex was irradiated at 360 nm. Analysis of the modification of the subunits showed that in the transcription active complex the β -subunit is modified within the limits of the 515–660 and 1091–1107 peptides and the β' -subunit is modified within the limits of the 400–465 peptide; in the inactive complex, only the β' -subunit is modified within the limits of the 1091–1107 peptide.

Other less traditional approaches to the study of the active centres of RNA polymerase have been developed recently. Thus it has been proposed⁵¹ that the chemical and genetic approaches be combined in order to establish the region where the Mg^{2+} ion is bound in the active centre of the enzyme with replacement of the Mg^{2+} ion by Fe^{2+} . It was found that oxidative degradation of both the template and the enzyme takes place in this instance. The degradation proved to involve mainly the β' -subunit, cleavage occurring within the limits of the peptide located between the 466 and 400 methionine residues. Since the conservative sequence (*i.e.* a sequence characteristic of a wide variety of nucleic acid polymerases) NADFDGD (in terms of single-letter designations, N = asparagine, A = alanine, D = aspartate, F = phenylalanine, and G = glycine) is located on this section, it was concluded that the above fragment participates in the binding of the magnesium ion. A mutant variant of RNA polymerase, in which the β' -subunit contained in the same place the NAAFAGA sequence (the aspartate residues were replaced by alanine residues) was obtained by the protein engineering method for additional confirmation of the cleavage site. After the replacement of Mg^{2+} by Fe^{2+} , the enzyme was not cleaved in the presence of this fragment. The cleavage of template DNA at rigorously defined sections in the –1 and –2 positions relative to the transcription start point was observed in the same experiment.

The use of a chimeric reagent, consisting of the conjugate of the initiating substrate (ATP) with an antibiotic (rifampicin), for affinity modification has been described.⁵² This antibiotic is a powerful inhibitor of prokaryotic RNA polymerases and it is therefore an effective antitubercular preparation. A series of conjugates with different lengths of the $-NH-(CH_2)_n-NH-$ spacer, connecting the carboxy-group of the antibiotic with the ATP γ -phosphate, were prepared. It was found that, when the length of the linker is $n > 3$, the conjugate serves as the initiating transcription substrate, whereupon the optimum length of the spacer corresponds to $n = 5$. Rifampicin is known to be bound strongly to the enzyme. This means that the distance between the centres binding the antibiotic and initiating the substrate is ~ 1.5 nm.

A conjugate of the spacer of which included the alkylating group $-NH(CH_2)_2N[C(O)CH_2Br](CH_2)_6$ has also been synthesised. In this case, the modification of the transcribed DNA strand in the C(–3) and C(–2) positions was detected.

The authors also employed a procedure which they called a pseudoenzymic reaction. For this purpose, the alkylating fragment $-NH(CH_2)_nNHC(O)CH_2Br$ was attached to the carboxy-group of rifampicin and an ATP analogue, containing a sulfur atom instead of one of the oxygen atoms in the γ -phosphate, was introduced into the reaction mixture containing the enzyme and the rifampicin derivative. When these compounds were disposed favourably in the corresponding active centres, the alkylation of the thio-analogue of ATP was observed. The most effective alkylation was noted for $n = 4$, which corresponds to the size of the spacer with six carbon atoms.

Nucleoside triphosphates can function in the transcription process in ways other than as substrates of the polymerisation process. In the study of the photoaffinity modification of RNA polymerase II from calf thymus with the aid of 8-azido(naphthalene-1'-sulfonyl) [α -³²P]ATP, it was established that, when one residue of the reagent is attached covalently, modification accompanied by the complete inactivation of the enzyme takes place. The inactivation occurs competitively in relation to ATP. However, other substrates — CTP and GTP — are not competitive

inhibitors in relation to the reagent and hence the modified section is not a substrate binding site. Since for the initiation of the transcription by RNA polymerase II the hydrolysis of one ATP group is required, it has been suggested that the modification takes place at a specific ATP binding site in which the hydrolysis required for the initiation occurs.⁵³ Using the 2'-*O*-dansyl-ATP fluorophor, which according to the authors forms a complex with the modified enzyme at the substrate binding site, it was possible to determine the distance between the ATP and the other substrate binding site, by measuring the resonance energy transfer. It was found to be ~2.5 nm.

All the methods described above lead to the labelling of the enzyme in the NTP binding region. There have been individual studies in which an attempt was made to bind the enzyme to the 3'-end of the growing RNA chain. The syntheses of several short transcripts into the 3'-ends of which the s⁴UMP residue had been introduced have been described.⁵⁴ Short single-stranded templates with the general structure (3')d(CCCCCGCTTGTGGTG – X), where X = A, TA, TTA, or TTTA, were used for this purpose. They were transcribed with the aid of yeast RNA polymerase I in the presence of the GpCpG primer and three substrates: ATP, [α -³²P]CTP, and s⁴UTP (the transcribed part of the template is underlined). It is not difficult to note that the transcription began with the site where the 3'-end of the primer is located and, since there is a single dA residue on the transcribed strand, located at the 5'-end of the template, a single s⁴UMP residue, coded for by this dA, was incorporated in the 3'-end of the transcript. After the completion of the process, the transcripts obtained, with a length equivalent to 12–15 nucleotide residues, were found to be part of the composition of the transcription complexes containing the enzyme, the template, and the transcript with a photoreactive residue located in the region of the active centre. Irradiation led to the attachment of the radioactive label to two subunits with molecular masses of 190 and 135 kDa. The ratio of the levels of radioactivity of the two subunits changed as a function of the length of the transcript, although it would seem that in all the systems investigated the photoreactive residue has always been in the same position on the enzyme, corresponding to the 3'-end of the transcript. This is unexpected and has not found a convincing explanation.

The same approach with the same set of template and transcripts labelled at the 3'-end has been used for the affinity modification of RNA polymerase II from yeast and wheat seedlings. In both cases, the affinity modification led to the incorporation of radioactivity solely in the largest subunit (220 kDa for the yeast enzyme and 180 kDa for the enzyme from wheat seedlings).⁵⁵

IX. The study of the interaction of eukaryotic transcription factors with DNA

For each of the three eukaryotic RNA polymerases, there is an intrinsic set of transcription factors participating in the transcription initiation stage. In accordance with the number of the polymerase, they are designated as TFI, TFII, and TFIII. Within the limits of each set, they are additionally designated by Latin letters. The majority of the factors consist of several subunits. In the transcription of the genes of information RNA, the set of principal factors necessary for the transcription of any genes participates in the initiation, while additional highly specialised factors are needed to trigger a whole series of genes. The principal factors include TFIIA, TFIIC, and TFIID, which form a primary complex in the immediate vicinity of the section of DNA containing the d(TATA) sequence at a short distance upward from the start point of the transcription, as well as the factors TFIIIE, TFIIF, TFIIB, and TFIIH. One of the subunits of the last factor is a protein kinase and catalyses the phosphorylation of the large subunit of the RNA polymerase, which is necessary for the manifestation of enzyme activity.

Figure 5 presents a schematic illustration of the disposition of the subunits of the factors TFIIB and TFIIC on genes.

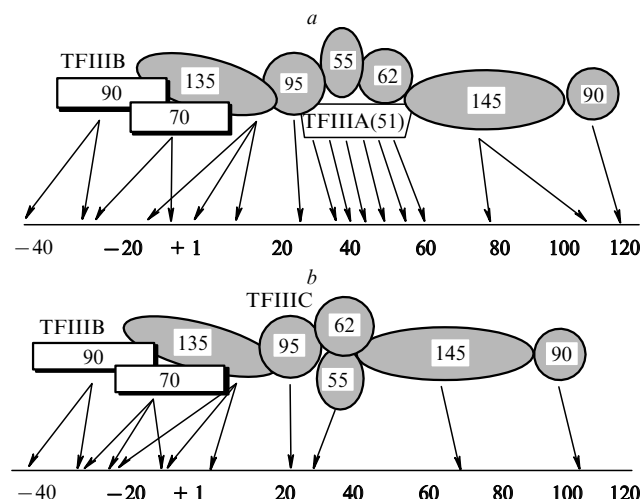


Figure 5. Schematic illustration of the interaction of the transcription factors III with the genes of 5S rRNA (a) and the 4th suppressor tRNA^{Tyr} (b). The masses of TFIIA, TFIIB, and TFIIC are indicated in kDa. The arrows indicate the position in the DNA sequence which have been photocross-linked with a particular subunit of the transcription factors.

A detailed arrangement of the subunits on two DNA specimens coding respectively one of the tRNAs and ribosomal 5S RNA has been established for the factors TFIIC with the aid of photoaffinity modification. The disposition of part of the promoter region within the limits of the coding section is characteristic of RNA polymerase III. A large series of double-stranded DNA have been obtained by genetic engineering techniques.^{56,57} One of the strands was elongated by several units with the aid of DNA polymerase with incorporation into the mixture of the elongating substrates of a photoreactive dNTP — 5-(3-*p*-azido-benzoylaminoallyl)dUTP. The photoreactive label was introduced in this way into various positions in DNA, after which a complex with the corresponding factors was formed, the photoaffinity modification of the factors was carried out, and it was established to which genes the covalent binding had taken place.

X. Conclusion

The methods based on chemical modification began to be applied to template biosynthesis systems primarily on ribosomes. The first studies of the modification of the tRNA binding region with the aid of an alkylating derivative of tRNA and of the mRNA binding region with the aid of an alkylating derivative of an oligonucleotide were published at the beginning of the 1970s.^{58,59} These were followed by systematic investigations of the structural-functional topography of the *E. coli* ribosomes with the aid of photoreactive derivatives of tRNA and reactive derivatives of ribooligonucleotides (the main results of these investigations are presented in a review⁶⁰). In recent years, similar studies have been initiated on ribosomes from human placenta. Information has been obtained about the protein environment and the sections of ribosomal RNA in the region where genetic information is decoded.^{61,62} Bifunctional cross-linking methods have found extensive application in the determination of the steric organisation of ribosomes. They make it possible to determine the mutual disposition of the ribosomal proteins and their disposition relative to particular sections of ribosomal RNA. In combination with data on the mutual disposition of proteins found by the neutron scattering method, this made it possible to construct a detailed three-dimensional model of the disposition of the 16S ribosomal RNA in the small subunit of the *E. coli* ribosome.⁶³

From the data presented in the review, it is seen that the systematic application of chemical methods to the study of transcription has only just begun.

With the exception of the investigation of ribosomes, the bifunctional cross-linking method has not so far found extensive application in the study of transcription. As an individual example, mention may be made of the study⁶⁴ whose authors used a bifunctional reagent (*N*-hydroxysuccinimidyl-4-azidobenzoate) — to elucidate the interaction of the subunits of the *E. coli* RNA polymerase with the protein ω , which is present in a highly purified enzyme preparation in a stoichiometric amount but is not an essential component for transcription. Bifunctional cross-linking data have shown that the protein is bound to the β' -subunit of the whole enzyme. The bifunctional cross-linking method is particularly effective in the study of systems with a large number of proteins and nucleic acids and one may therefore expect that its importance will increase as one proceeds to the study of transcription in more complex systems, for example in complexes of chromosomal DNA with eukaryotic RNA polymerases and with a set of transcription factors, including those forming part of the composition of chromatin.

It is seen from the examples quoted that chemical approaches lead to new unique possibilities for the study of template biosynthesis. The possibility of investigating the mechanism of the search by the enzyme for points at which the functionally significant process begins,²⁰ the determination of the positions and dimensions of the unwound section of DNA on RNA polymerase and its migration in the course of transcription,²⁶ and the determination of the RNA exit corridor, *i.e.* of the actual 'track' of the migration of the product on the enzyme as it moves away from the catalytic centre where biosynthesis takes place, are the most impressive features at the present time.^{29–34} It is at present difficult to even imagine experiments not based on chemical approaches which would make it possible to look quite so deeply into the dynamic aspects of template biosynthesis. Some of the procedures described may be and are already employed for the study of the transcription process in cell organelles.^{35,36}

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Low-frequency vibrational spectroscopy of amides and urethanes

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Abstract. The application of the methods of low-frequency vibrational spectroscopy to studies of amides and urethanes including polyamides, polypeptides, and proteins is critically analysed. Special attention is concentrated on the spectroscopic studies of intermolecular interactions and in particular on spectral features of the intrinsic vibrations of hydrogen bonds. The methods are considered that allow one to identify experimentally the bands in the region of $90\text{--}130\text{ cm}^{-1}$ associated with the vibrations of the hydrogen bridge. The potential and limitations of the methods of low-frequency spectroscopy for the investigation of these classes of compounds are discussed. The bibliography includes 131 references.

I. Introduction

Compounds containing amide and urethane groups constitute an important class of substances that are widely used in the processing and production of polymeric materials (polyamides and polyurethanes), and are of special importance in molecular biology (polypeptides and proteins). Among the structural methods used for the investigation of the structure of these compounds, vibrational spectroscopy occupies a prominent position contributing to the solution of many problems in the physical chemistry and chemistry of polymers.¹

The so-called middle spectral region of vibrational frequencies, which is normally used, falls in the range of wavenumbers from $400\text{ to }4000\text{ cm}^{-1}$. The low-frequency spectral region, which lies below 400 cm^{-1} , is much less studied. Nevertheless, this interval, usually called the low-frequency region, allows one to gain information that is unavailable by other methods. Low-frequency spectroscopy is used in both the physics of solids, in the study of radiation absorption by magnetic, ferromagnetic semiconducting, and other materials,² and in physical chemistry, in the study of barriers to internal rotation, charge transfer

compounds, inorganic complexes, intermolecular interactions, vibrations of crystal lattices, *etc.*³

The low-frequency spectral region is of interest for the studies of amides and urethanes because first of all bending and torsional vibrations of the molecular skeleton manifest themselves in this region. These vibrations are especially sensitive to the spatial structure of molecules and to intermolecular interactions. It is in this region that the intrinsic vibrations of the hydrogen bond and intermolecular vibrations of crystal lattices are observed.

Three major experimental methods are used for the investigation of the low-frequency region of vibrational spectra, namely, far infrared spectroscopy (FIR),³ low-frequency Raman spectroscopy (Raman),⁴ and inelastic neutron scattering (INS).⁵ It is well known that IR and Raman spectroscopy are complementary to each other because the selection rules for symmetric molecular systems for the IR and Raman usually differ. However, even in the absence of symmetry, the combined use of these methods is very helpful, for there is no direct relationship between intensities in these two types of spectra. If, for example, in the IR spectrum a band of some vibration is weak and overlaps another band, it can manifest itself distinctly in the Raman spectrum, and *vice versa*. The INS method is less accessible to researchers, but it is attractive since there are no selection rules for these spectra, and in many cases the INS spectrum contains therefore more bands than the IR or Raman spectra. Recently FIR spectroscopy has gained wide usage for a number of experimental reasons. This is determined by the fact that since the 60s serial diffractive spectrometers for this region are being manufactured and, especially, in the context of the development of Fourier spectroscopy, which covers the low-frequency region of the spectrum, too.

There is no difference in principle in the approaches to the interpretation of the spectra in the middle and far regions: normal coordinate analysis, the method of group frequencies (though in the low-frequency region this method has a limited application because organic compounds seldom have group bands in this region), the method of examination of isotopically-substituted compounds, and some other methods are used in both cases. However, there are specific features in the low-frequency region consisting, first of all, in the fact that intermolecular vibrations manifest themselves in this region (as has already been mentioned), which is primarily typical of crystalline compounds and some associated liquids. Therefore, for normal coordinate analysis of crystals in both middle and far frequency regions, strictly speaking, the structure and symmetry of the crystal lattice should

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be considered. A numerical calculation of frequencies is substantially complicated due to the large number of atoms that are to be taken into account. These calculations are possible and are being conducted⁶ for crystals of low-molecular-weight compounds, whereas in the case of polymeric molecules, they can be performed only for the polymers with simple structure such as polyethylene⁷ and polypropylene.⁸

The following approach is used as a rule for the interpretation of the spectra of crystalline polymers. A normal coordinate analysis is run for an isolated chain; sometimes, for polypeptides and proteins with the helical structures, the hydrogen bonds stabilising these structures are taken into consideration. Then, the symmetry of the crystal lattice is analysed, and the number and activity of the expected intermolecular vibrations is determined from the group theory. The assignment of these vibrations in the spectrum is usually made empirically on the basis of selection rules, polarisation, *etc.*, though the methods of approximate calculations of the frequencies have been developed for intermolecular vibrations.⁶

A fairly complete bibliography (up to 1969) covering all the problems of FIR spectroscopy has been compiled by Bloor.⁹ Unfortunately, more recent publications,^{10–13} in which FIR spectroscopy of organic and in particular polymeric compounds have been considered, are incompatible with the above-mentioned review⁹ in the scope of problems and coverage of references. To our knowledge, there are no reviews devoted especially to low-frequency Raman spectroscopy.

The purpose of the present review is the consideration and systematisation of the principal results accumulated to date of investigations concerning the application of low-frequency spectroscopy to the studies of amides and urethanes. The range of problems associated with the band assignment in this region is defined.

In most cases, the interpretation of low-frequency spectra is a rather complicated task. Vibrations of the bonds between heavy atoms, skeletal, bending, and torsional vibrations sensitive to the spatial structure and intermolecular association, vibrations of crystal lattices and polymeric chains, and the intrinsic vibration of the hydrogen bond are located in this frequency region. In each specific case, the band assignment most often requires special investigations. As intermolecular interactions are of special interest for the studies of amides and urethanes, let us dwell on the methods of identification of the bands originating from the vibrations of hydrogen bonds.

II. Methods for the assignment of bands in the low-frequency region of vibrational spectra to the hydrogen bond modes

The absorption bands sensitive to the presence of hydrogen bonds can be identified if the hydrogen bond is fully or partially broken or somehow changed. Dilution is one of the methods used to this end. Thus the analysis of the vibrational spectra of solutions, in which the hydrogen bond in the compound under study is broken upon dilution in the middle IR region of vibrational frequencies allows one to make a definite conclusion on the presence or the absence of H-bonds. However, the application of the dilution method in the low-frequency region is markedly complicated for it is impossible to measure FIR spectra at low concentrations. If thick layers are used, weak bands corresponding to H-bonds are obscured by the bands associated with strong absorption by the solvent.

Hydrogen bonds are more often studied by the method of dissolution in polyethylene matrices.¹⁴ This method has been developed specially for the FIR region as polyethylene is practically transparent in the low-frequency region. The spectra of compounds measured in the polyethylene matrix at room temperature and at the temperature of liquid nitrogen correspond to the 'normal' spectra of these compounds in solutions of different

concentrations. This phenomenon has been used by Jakobsen and Brasch¹⁵ in the investigation of hydrogen bonds in phenol derivatives. It was found that when phenol adsorbed as a polymer with hydrogen bonds was slowly heated, it was transformed into a monomeric form as a result of H-bond cleavage and, on the contrary, cooling restores the system of hydrogen bonds. Thus, 'dilution' can be achieved by changing the temperature.

The method of matrix isolation¹⁶ is rather efficient. The principle of this method is to hold the molecule in a solid inert medium at temperatures that are sufficiently low to prevent translational motions of the molecules. Knozinger and Schrems¹⁷ have reviewed the data on the studies of hydrogen bonding obtained by FIR spectroscopy.

The phenomenon of a change in the H-bond strength with temperature and pressure is also used for studies of hydrogen bonding. High sensitivity of the hydrogen bonds to temperature results from an equilibrium shift of the process of H-bond formation, which leads to a change in the proportion of the groups taking part in the intermolecular interaction. This causes substantial changes in the spectra in the frequency region corresponding to vibrations of the groups involved in the hydrogen bond formation, which is normally used as the key criterion for the presence of the hydrogen bond.¹⁸ The application of the technique of high pressures in spectral studies also provides a possibility to reveal changes in the bands sensitive to the hydrogen bond, since high pressure (up to 160 000 atm) affects intermolecular interactions and hence their vibrational characteristics.³

The deuteration method is widely used for the assignment of bands in the middle IR region to the modes involving the hydrogen atom. In the spectra of deuterated analogues, the frequencies associated with the vibrations of the hydrogen atom are always shifted. However, in the low-frequency region of the spectrum, deuteration is not so efficient and does not always lead to the desired result, since the frequency shift for the bands of the hydrogen bond is 1–5 cm⁻¹ (see Ref. 19) and sometimes is not observed at all. This originates from the fact that this is not the vibration of the hydrogen atom relative to the proton acceptor but that of the proton donor relative to the proton acceptor. However, if this small frequency shift does take place, the FIR method registers it quite reliably.

Comparative analysis of the spectra of a series of related compounds is often applied to interpret the spectra. For example, comparison of the FIR spectra of a series of carboxylic acids allowed one to distinguish the bands belonging to the hydrogen bond from those associated with intramolecular modes.²⁰ The application of this method along with other methods to polymeric systems also gives positive results.²¹

Reliable data on the assignment of a band to the vibration of the hydrogen bridge can be obtained by replacing the hydrogen atom by a group that does not form a hydrogen bond. This method was used in studies of the inherent modes of the hydrogen bond in the simplest amides.²²

In the case of anisotropic systems such as oriented polymers, monocrystals, definite information can be gained from the polarised spectra. In the majority of cases, the direction of the hydrogen bond is close to that of the A–H valency bond. The knowledge of the structure of the anisotropic system and the dichroic ratio of the bands allows the proposed assignment to be proved or demolished. This method is widely used in studies of oriented polymeric systems in the middle IR region²³ and sometimes in the low-frequency region.¹²

As for low-frequency Raman spectra of liquid systems, the difficulties in their measurement is associated with the large half-width of the band due to Rayleigh scattering. Nielsen²⁴ has developed the technique of the *R*(*v*) representation for the low-frequency Raman spectrum, which permits subtraction of the background of the Rayleigh scattering so that a rather distinct low-frequency spectrum can be obtained, which can be successfully compared with the FIR spectrum. According to this technique, the spectrometer is connected with a computer and

processing of the spectra is carried out automatically. Nielsen and co-workers have performed a series of investigations by means of the $R(\nu)$ representation; in particular, low-frequency Raman spectra for compounds containing the amide group have been studied. This method is especially valuable because it allows the investigation of biological systems in aqueous solution.

Naturally, it is desirable to use a complex of the methods described to obtain reliable results.

Definite progress can be achieved in the studies of intra- and intermolecular vibrations if experimental results are supplemented with theoretical calculations. The number, type, character, and optical activity of the intermolecular modes can be predicted from theoretical calculations for crystalline systems.^{6,25} At present, methods for calculation of these frequencies have been developed. Service programmes are available for these calculations on big and personal computers.^{26,27}

III. Low-molecular-weight amides

The simplest secondary amide, *N*-methylacetamide (*N*-MAA), is often considered as a model of an amide unit in polyamides, polypeptides and proteins. This is the reason for an interest in the investigation of its structure. Numerous papers are devoted to the study of the vibrational spectra of *N*-MAA. These investigations were started in the 50s and are still in progress.

It is well known that *N*-MAA is liquid at temperatures above 28 °C; in the solid state it can exist in two crystalline forms:²⁸ as a disordered crystal in the temperature interval from 28 to 10 °C, and as an ordered crystal at temperatures below 10 °C. The skeleton of the molecule has a planar structure with a *trans*-arrangement of the carbon atoms of the two methyl groups.²⁸ However, the presence of the *cis*-form is also suggested, which allows the fine structure of vibrational bands to be explained.²⁹

The vibrational spectra of *N*-MAA have been well studied both experimentally and theoretically. The characteristic bands of the modes of the amide group have special names from 'Amide I' to 'Amide VII'.¹

Since *N*-MAA is convenient as a model compound, recently a normal coordinate analysis has been performed in detail for this compound^{30–32} in order to obtain the force field that can be applied to calculations of the spectra of polypeptides and proteins.

The FIR spectra of *N*-MAA and related compounds were first studied by Itoh and Shimanouchi.³³ Two bands at 201 and 102 cm^{−1} are observed in the FIR spectrum of liquid *N*-MAA (Fig. 1). The authors assign the band at 201 cm^{−1}, which is shifted to 185 cm^{−1} upon deuteration of the methyl groups, to the torsional mode about the C–N bond. The absorption at 102 cm^{−1} is associated with the intrinsic mode of the hydrogen bond. This assignment is based on the fact that this band, which is typical also of other simple amides,²² is shifted by *ca.* 3–4 cm^{−1} upon deuteration of the NH-group and disappears upon replacement of the hydrogen atom at the nitrogen by another group (Fig. 1). The deuteration of the methyl groups does not affect the frequency of this mode.

The data obtained from the FIR spectra are confirmed by investigations of the low-frequency Raman spectra of *N*-MAA,^{34,35} which, in particular, show that the band in the region of 100 cm^{−1} is shifted to the low-frequency region as the temperature increases (Fig. 2). The authors^{22,34} believe that the *N*-MAA molecules in the liquid state form linear chains *via* hydrogen bonds and have a structure close to that of the disordered crystal phase.

The problems of association of the *N*-MAA molecules in the liquid state and in CCl₄ solution have been discussed in more detail.^{36–38} A detailed analysis of frequencies and intensities of the amide associates formed *via* the hydrogen bonds has been performed on the basis of normal coordinate analysis and an experimental study of the IR spectra of *N*-MAA in solution.³⁶ A force field and a set of electrooptical parameters were proposed for H-bonded associates of *N*-MAA molecules. The complex

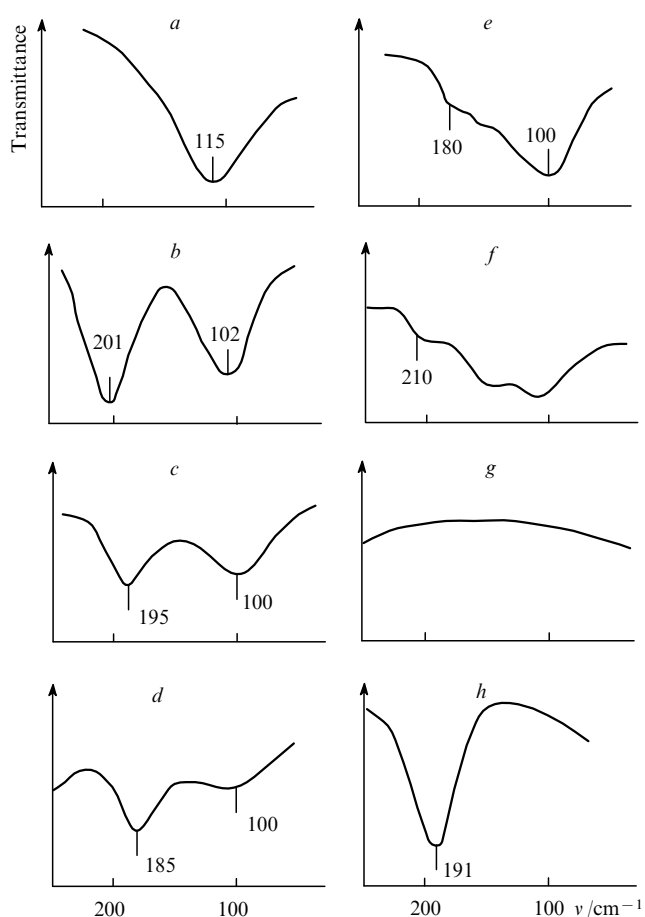


Figure 1. The FIR spectra of model amides and related compounds.³³ (a) HCONHCH₃, (b) CH₃CONHCH₃, (c) CD₃CONHCH₃, (d) CD₃CONHCD₃, (e) EtCONHCH₃, (f) CH₃CONHEt, (g) HCON(CH₃)₂, (h) CH₃COOCH₃.

contour of some bands 'Amide I', 'Amide II' in solution might be rationalised by the existence of associates of various length.

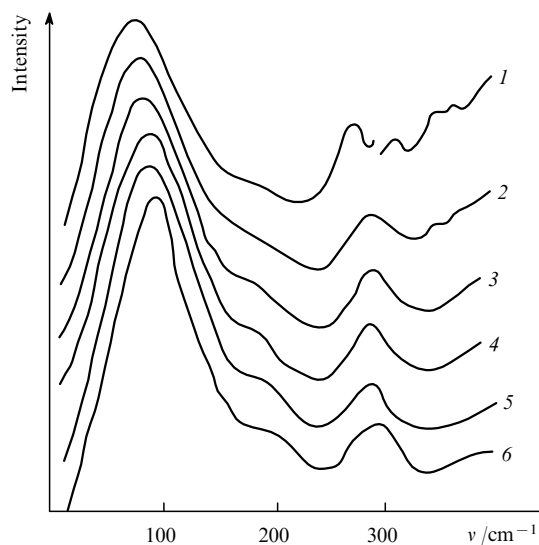
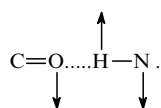


Figure 2. The smoothed $R(\nu)$ spectrum of liquid *N*-MAA at different temperatures (°C): (1) 165, (2) 150, (3) 120, (4) 90, (5) 60, (6) 30.

The comparison of absorption bands in the middle IR region in the spectra of tetramer, pentamer, and hexamer shows that a specific saturation of the frequency shifts takes place as the degree of association increases, then only the band contour changes.³⁷ On the contrary, in the FIR region where the bands of the hydrogen bond modes are located, a systematic shift to the low-frequency region occurs with an increase in the number of molecules in the complex. According to calculations of the frequencies for the final chains, the dependence of the frequency on the number of the *N*-MAA molecules in the associate manifests itself well in the range of the NH stretch (3348, 3338, 3334, and 3330 cm⁻¹ for *n* = 2, 3, 4, and 6, respectively) and in the FIR region, where the intrinsic vibration of the H-bond manifests itself (121, 105, 101, and 98 cm⁻¹ for *n* = 2, 3, 4, and 6, respectively). The comparison of the calculated frequency for the hydrogen bond vibration with that in the experimental spectra makes it possible to estimate the size of associates in liquid *N*-MAA (*n* = 2–6).

The complex structure of the amide bands can alternatively be explained by assuming that *cis*- and *trans*-isomers coexist in solutions of *N*-MAA,³⁸ which is based on examination of the spectra of solutions at various temperatures and concentrations. The 'Amide I' band was separated into four Gaussian components, which the authors relate to the *cis*- and *trans*-isomers of *N*-MAA. However, from our viewpoint these results do not contradict the explanation of the complex contours of the bands by the existence of associates of different length.^{36,37} Moreover, the dependence of the enthalpy of the hydrogen bond formation on the chain length of associates is proposed,³⁸ which cannot but influence the frequencies of the 'Amide I' and 'Amide II' bands.

ab initio Calculations performed by Nielsen²² as well as normal coordinate analysis for the *N*-MAA molecules³³ indicate that the band at 100 cm⁻¹ is the bending vibration of the hydrogen bond of the type



The crystalline *N*-MAA was studied by FIR,³³ Raman,³⁹ and INS⁴⁰ spectroscopy in the low-frequency region. On going from liquid to disordered crystal, the frequency of the hydrogen bond mode in the IR spectrum³³ shifts from 102 to 125 cm⁻¹ (Table 1). The passage to the ordered crystal results in its further shift to 130 cm⁻¹ and a new band appears at 90 cm⁻¹, the intensity of the latter increasing with a decrease in temperature. Simultaneously, the band at 201 cm⁻¹ shifts to higher frequencies and splits into two components at 221 and 243 cm⁻¹. The crystal existing at temperatures below 10 °C exhibits two torsional vibrations (*A*₂ and *B*₂) about the C–N bond. For structures of *C*_{2v} symmetry, the *A*₂ mode is inactive in the IR, and the appearance of two torsional modes about the C–N bond means that the structure of the crystal unit of *N*-MAA deviates from this group symmetry.

Normal coordinate analysis³³ for the crystal lattice of *N*-MAA with consideration of the hydrogen bond confirms the presence of two torsional modes in the crystal: 205 (*A*₂) and 227 (*B*₂) cm⁻¹. In addition, it is shown that the band in the region of 130 cm⁻¹ is associated with librational lattice modes and that in the range of 90 cm⁻¹ belongs to translational lattice vibrations. Hence, according to the data from Ref. 33, temperature changes

Table 1. The frequencies (ν/cm⁻¹) of H-bond bands in the spectra of *N*-MAA in the region of 30–300 cm⁻¹.

Phase state of <i>N</i> -MAA	Method	Temperature / °C	ν in the region		Ref.
			100 cm ⁻¹	200 cm ⁻¹	
Liquid	Raman	30	102	201	35
Disordered crystal	IR	15	125	201	33
Ordered crystal	IR	10	130	210	33
			90		
	IR	–80	132	221	
			90	243	

in the crystal affect the frequency shift for the torsional vibration much more significantly than the frequency of the hydrogen bond vibrations (see Table 1).

The Raman³⁹ and INS⁴⁰ spectra of crystalline *N*-MAA and its isotopomers supplement information from the IR spectra. The frequencies observed in the IR, Raman, and INS spectra of crystalline *N*-MAA³⁹ are presented in Table 2. About 10 lines are recorded in the region below 200 cm⁻¹ in the Raman spectrum. The authors³⁹ believe that the lattice modes (external vibrations) are in the region below 110 cm⁻¹ because isotopic substitution has little influence on the frequencies of these bands; the torsional vibrations about the C–N bonds manifest themselves in the region of 120–170 cm⁻¹. Calculation of the potential function for this torsional vibration revealed two symmetric energy minima separated by a small potential barrier, which suggests that the skeleton of the molecule is non-planar. Provided this result is applied to the peptide group, this can be important for understanding the physicochemical properties of polypeptides and proteins.

Formamide and its derivatives have been studied in the liquid by the method of the *R*(ν) representation (Raman) in the low-frequency region.^{34,41,42} The conclusions on the structure of H-bonded chains of formamide are analogous to the results obtained for *N*-MAA. The bands in the region of 150–200 and 110 cm⁻¹ observed for formamide are interpreted as librational modes of the molecules associated *via* the hydrogen bonds, which is in accordance with the data on degrees of the line depolarisation, temperature measurements, and the spectra of solutions.

IV. Polyamides

A large body of publications is devoted to investigations of polyamides by IR spectroscopy in the middle frequency region (see, for example, Refs 1, 43, and references cited therein) in which the problems of the structure and orientation of molecules, the hydrogen bond formation, *etc.* have been discussed. However, there are relatively few publications on the FIR spectra of polyamides. The emphasis is on revealing the correlation between the FIR spectra of polyamides and the conformations of the molecular backbone, because a number of skeletal and torsional bands sensitive to conformations are located below 700 cm⁻¹.

Nylons are known to exist in three crystalline modifications. In the α- and β-forms, planar extended chains have the *trans*-

Table 2. The comparison of frequencies and intensities of the bands in the IR, Raman, and INS spectra for *N*-MAA.

Method	T/K	ν/cm^{-1} ^a								Ref.	
IR	93	130 s								90 s	33
Raman	35	164 s		127 s	105 vs	98 sh	91 m	73 w	65 w	39	
INS	5	164 s	153 s	126 w	104 w		87 w		62 vw	40	

^a Accepted notations for band intensities: vs is very strong, s is strong, m is medium, w is weak, vw is very weak, sh is shoulder.

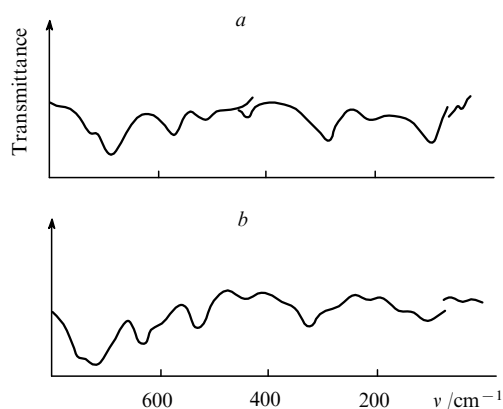


Figure 3. The IR spectra of the α - (a) and γ -forms (b) of nylon-6.⁴⁵ Hereinafter gaps in the spectra are connected with the special features of the equipment used: with changing of diffraction gratings, filters, changes in the thickness of the samples, etc.

conformation, in the γ -modification chains are turned about ordinary bonds neighbouring the amide groups.

A series of various kinds of nylons has been studied by the FIR^{44,45} and INS⁴⁶ methods. The IR spectra of nylon-6 in the α - and γ -modifications⁴⁵ are presented in Fig. 3. It is seen that the spectra in the low-frequency region differ substantially. Analysis of the spectra of 18 polyamides (nylons- n,m and nylons- n) made it possible to reveal the common bands typical of the planar and non-planar conformations and to give an empirical assignment for a number of bands (Table 3).⁴⁴ The difference in chain conformations is responsible for the different frequencies of such bands as 'Amide V', 'Amide VI', and 'Amide VII', which manifest themselves in the regions 700, 600, and 230–300 cm^{-1} , respectively. The bands associated with bending and torsional modes of the amide and methylene fragments of the chains appeared to be sensitive to chain rotation.²¹ The examination of the 'Amide VII' bands sensitive to conformation and bending vibrations in the range of 300 cm^{-1} allowed one to investigate chain conformations in polyamide fibres and fabrics, in particular, for nylon-6 depending on the method of sample preparation.⁴⁷ The 'Amide VII' mode for the pseudo-hexagonal crystal structure has a frequency of 205 cm^{-1} . It is noted that the X-ray diffraction method cannot distinguish satisfactorily the crystalline forms of nylon-6, in this case FIR spectroscopy appears to be very useful.

Table 3. The low-frequency absorption bands (cm^{-1}) of the amide groups for polyamides in various crystalline forms.

α -Form	γ -Form	Assignment ^a
690	715	'Amide V' (γ , NH)
580	630	'Amide VI' (γ , C=O)
360	—	Deformation of the skeleton —CH ₂ —CONH—CH ₂ —
230	300	'Amide VII' (τ , CONH)

^a γ is out-of-plane modes, τ is torsional modes.

Jakes and Krimm⁴⁸ have performed normal coordinate analysis for a series of amides and polyamides. They calculated the valence-force field for this class of compounds. The calculations performed for a series of molecules containing the amide groups fit well the experimental spectra in the middle region of frequencies. No detailed analysis of the low-frequency region has been carried out, the authors only mentioned that skeletal and torsional vibrations of the chain manifest themselves in the region below 500 cm^{-1} .

Tadokoro *et al.*²¹ calculated the frequencies in the far region for nylon-6 having the planar conformation of the chain (α -form). Besides nylon-6, these authors studied a series of polyesters [$-(\text{CH}_2)_m-\text{CO}-\text{O}-$]_{*n*} ($m = 1, 2, 4, 5$) having the planar zigzag structure in the crystalline state. The absorption bands in the spectra of the polyesters studied and nylon-6 appeared to be related to similar modes. Comparative interpretation of the spectra of these compounds was made on the basis of band calculations²¹ (Table 4). It was shown that bending and torsional modes of the chain backbone and the amide group are located in the region below 700 cm^{-1} .

Table 4. The assignment of group bands in the spectra of aliphatic polyesters and nylon-6.²¹

Frequency / cm^{-1}	Band assignment ^a	
	aliphatic polyesters	nylon-6 (α -form)
730–630	$\delta(\text{C}=\text{O})$, $\nu(\text{CH})$, $\delta(\text{skeletal})$	—
690	—	'Amide V'
590–580	$\gamma(\text{C}=\text{O})$	'Amide VI'
523 ^b	$\delta(\text{CH}_2-\text{CO}-\text{O})$, $\delta(\text{skeletal})$	$\delta(\text{CH}_2-\text{CO}-\text{N})$, $\delta(\text{skeletal})$
450–430	$\delta(\text{OCH}_2-\text{CH}_2)$, $\delta(\text{CH}_2-\text{chain})$	$\delta(\text{NCH}_2\text{CH}_2)$, $\delta(\text{CH}_2-\text{chain})$
370–295	$\delta(\text{CHCOOCH})$, $\delta(\text{CH}_2-\text{chain})$	$\delta(\text{CHCONHCH})$, $\delta(\text{CH}_2-\text{chain})$
233–195	$\tau(-\text{CO}-\text{O}-)$, $\tau(\text{CH}_2-\text{chain})$	$\tau(\text{CH}_2-\text{chain})$
150–90	$\tau(\text{CH}_2-\text{chain})$, $\tau(-\text{CO}-\text{O}-)$	$\tau(\text{CH}_2-\text{chain})$

^a Accepted notation (here and in Tables 5 and 6): ν is stretching, γ is out-of-plane, δ is bending, τ is torsional vibrations. ^b This band appears when the number of the CH₂ groups exceeds 5.

A normal coordinate analysis has been performed for isolated chains.²¹ The spectra measured at the temperature of liquid nitrogen appeared to be similar to those taken at room temperature, and the intermolecular modes did not manifest themselves in the experimental IR spectrum.

The band observed in the region of 100 cm^{-1} is believed to be associated with the coupled torsional vibrations of the methylene chains and the amide group. This band has a complex contour, its frequency shifts somewhat upon deuteration of the NH group and becomes more intense when the samples underwent annealing and thermal treatment. From these facts, the data from the studies of low-molecular-weight amides, and the fact that the paper cited reports the spectra of films,²¹ which doubtless contain the bands of the hydrogen bond, it was reasonable to assign the band in the region of 100 cm^{-1} (or, probably, one of its components) to a mode of the hydrogen bond.

It was this interpretation that was given by Frank and Fiedler⁴⁹ who considered the IR spectra of nylons in the region of 20–400 cm^{-1} . They assigned the absorption band in the region of ca. 100 cm^{-1} in all the spectra examined to the translational motion of the bonded amide groups of neighbouring chains, which they represented by the model of coupled oscillators. The frequency of this band is practically the same in the spectra of α - and γ -nylons despite the difference in conformations of the macromolecules. It can only be noticed that the half-width of the band is somewhat smaller for α -nylons.

An attempt to study moments of inertia for a repeating unit of the polymeric chain has been made on the basis of the data on the frequencies of the absorption bands assigned to the torsional modes about the C–N bond.⁴⁹ The bands at 630 cm^{-1} (nylon-2),

374 cm^{-1} (nylon-4) and 291 cm^{-1} (nylon-6) were assigned to the torsional modes about the C—N bond, the decrease in the frequency with the chain length increase was explained by the dependence of the absorption frequency on the moment of inertia of a repeating unit of the polymer. However, on going to nylons with a longer repeating unit, further decrease in the frequency was not observed. In this case, the determination of the moments of inertia for repeating units can hardly be considered correct because the band assignment is not justified, and the frequencies 630 cm^{-1} and 374 cm^{-1} are too high to be assigned to the torsional modes about the C—N bond.

Fibres of poly-*p*-phenyleneterephthalamide (Kevlar-49), the representative of aromatic polyamides, have been studied by FIR spectroscopy.^{47, 50} The FIR spectra of oriented samples in polarised light are reported without any band assignment,⁴⁷ and an attempt to interpret the spectra is made.⁵⁰ The bands were assigned (Table 5) taking into consideration data on the band dichroism and comparing the spectra obtained with those for the model low-molecular-weight substance, benzanilide, in the condensed state and in solution. The assignment of the bands associated with the intramolecular modes of the amide group in the low-frequency region is, in general, in accordance with the data on nylons. However, the assignment of the bands associated with the intermolecular vibrations raises some difficulties. For example, the bands at 253, 287, and 305 cm^{-1} assigned to external vibrations have too high frequencies for a repeating unit of such a large mass.

Table 5. The absorption bands in the IR spectra of benzanilide and poly-*p*-phenyleneterephthalamide (fibre 'Kevlar-49')⁵⁰ in the region of 30–400 cm^{-1} .

Benzanilide	Kevlar-49	Dichroism	Assignment ^a
solu- tion	condensed state	fibre	
Intramolecular modes			
109	108	112	$\pi + \sigma$ $\tau(\text{C}_p\text{—NH}) + \delta(\text{CONH})$
180	184	198	$\pi > \sigma$ $T'(A') + \delta(\text{C}_p\text{—CONH—C}_p)$
209	202	216	$\sigma > \pi$ $\tau(\text{C—N})$
295	307	331	$\pi + \sigma$ $\delta(\text{CONH})$
356	370	348	$\pi > \sigma$ $\delta(\text{C}_p\text{—CONH—C}_p)$
Intermolecular modes			
—	61	67	$\pi + \sigma$ $T'(A'')$
—	90	83	$\pi + \sigma$
—	138	138	$\sigma > \pi$ $R'(A')$
—	160	160	$\sigma > \pi$ $R'(A'')$
—	240	253	$\pi > \sigma$ $R'(A' + A'')$
—	263	287	$\pi + \sigma$ with the participation of H-bond
—	305	305	$\pi + \sigma$

^a Mode: *T* — translational, *R* — librational.

Hence, the investigation of the FIR spectra and normal coordinate analysis for polyamides allowed the interpretation of these spectra. The features of the hydrogen bond in the low-frequency region are considered, and the bands sensitive to chain conformations are revealed. This provided a possibility to apply the low-frequency region of the spectra for analytical purposes.

V. Polypeptides and amino acids

The interest in the structure of amino acids and polypeptides stems from the rapid development of molecular biology. The knowledge of the structure of amino acids gives the key to understanding the structure of proteins. The application of molecular spectroscopy

to the studies of biological systems started in the 60s. Since that time, a number of monographs^{51–53} and reviews^{54, 55} has appeared reflecting the situation in this field. The problems of molecular spectroscopy of amino acids in the middle frequency region are discussed in the monograph by Parker.⁵⁶

The examination of the low-frequency region of the spectrum is of interest, first of all, from the viewpoint of investigation of intermolecular modes including the intrinsic modes of the hydrogen bond. Series of amino acids such as glycine, D,L-alanine, D,L-leucine, and others have been studied.⁵⁷ The authors have clearly demonstrated the advantages of low-temperature spectral investigations by showing distinct shifts of the bands belonging to intermolecular modes with a decrease in temperature (Fig. 4). Assuming that the frequencies of torsional vibrations depend on temperature, the bands in the region of 500 and 200 cm^{-1} , which are 10–20 cm^{-1} shifted upon cooling to 113 K, were assigned to the torsional modes of the NH and C—C groups, respectively. The bands in the region of 100–130 cm^{-1} , which are less shifted (by 5–7 cm^{-1}), were assigned to the stretch of the NH...O hydrogen bridge.

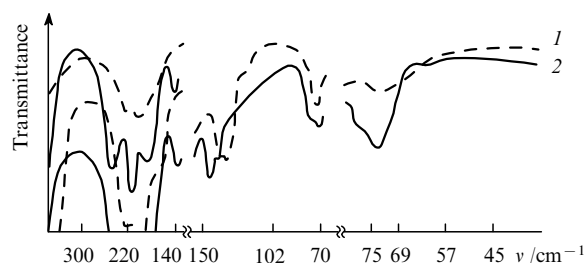


Figure 4. The FIR spectrum of α -glycine at 298 K (1) and 113 K (2).⁵⁷

The FIR spectra of crystalline L-alanine have been comprehensively studied.^{58, 59} Using the method of deuteration, temperature measurements, and normal coordinate analysis for crystalline L-alanine, Bandekar *et al.*⁵⁹ reported a detailed assignment of the bands observed in the IR and Raman spectra of crystalline L-alanine in the region of 40–500 cm^{-1} . The calculations showed that the vibration of the hydrogen bond manifests itself at a frequency of 146 cm^{-1} , it contributes, however, to other vibrational modes with frequencies of 110–150 cm^{-1} . The correctness of the assignment of the bands associated with the vibrational modes of the hydrogen bonds is proved by their small shift (3 cm^{-1}) upon deuteration of L-alanine, which, as was mentioned above, is typical of amides. The plot of the dependence of the position of the peak at 146 cm^{-1} on temperature is depicted in Fig. 5. On the basis of these data, the authors

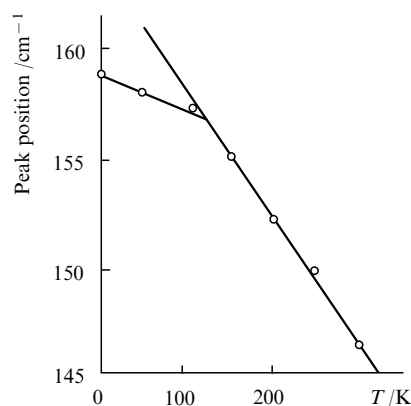


Figure 5. Temperature change in the position of the peak at 146 cm^{-1} in the IR spectrum of crystalline L-alanine at 300 K.⁵⁹

have performed the calculation of vibrational frequencies in the spectrum of L-alanine at 6 K. In this way the authors could follow the change in the potential energy of the crystal as the temperature decreases.

The comprehensive investigation of the spectra of low-molecular-weight amides and polyamides permitted a relatively simple progression to the interpretation of the spectra of polypeptides with the aim of establishing their structure. The bands of the amide modes such as 'Amide I' and 'Amide II' in the IR spectra and 'Amide I' and 'Amide III' in the Raman spectra (the 'Amide II' line is weak in the Raman spectra) are the main tool in this case. Although these bands reflect the structure of polypeptides, the molecules of which can exist in the helical and planar extended forms, the spectral features of different conformations can be substantially supplemented by the data on the low-frequency spectra as the low-frequency modes are especially sensitive to chain conformations. In addition, in a number of cases, low-frequency modes make it possible to quantify the content of different conformers because the bands in the low-frequency region associated with different chain conformations do not overlap neighbouring bands whereas the amide bands in the middle region, as a rule, overlap one another.

Polyglycine $(-\text{NH}-\text{CH}_2-\text{CO}-)_n$ is a polypeptide of the simplest structure, which can also be considered as a polyamide. Polyglycine exists in two crystalline modifications differing in the chain structure: polyglycine-1 (PG-1) with the planar chain conformation and polyglycine-2 (PG-2) with the helical structure. This polypeptide has been well studied by the methods of vibrational spectroscopy.¹ Thus the existence of two rotameric structures was first predicted from the data of IR spectroscopy.⁶⁰

The FIR spectrum of polyglycine was first studied by Miyazawa,⁶¹ who found that the spectra of PG-1 and PG-2 differ substantially. The INS spectra of polyglycine in the low-frequency region are reported.^{62,63} The availability of the IR, Raman, and INS spectral data has stimulated calculations of frequencies that have been carried out for both isolated chains⁶³ and crystals.^{64,65} Fanconi^{66,67} has performed an experimental and theoretical investigation of the low-frequency spectra of polyglycine in various forms and presented the most complete interpretation of the bands observed in the spectra.

Table 6 contains the assignment of the low-frequency modes for PG-1, which demonstrates the participation of the hydrogen bonds in vibrational modes in this region. As can be seen from Table 6, the band at 133 cm^{-1} observed in the FIR spectra of polyglycine is assigned to the nearly pure stretching vibration of the hydrogen bond as it accumulates 92% of the potential energy. An intense band at 82 cm^{-1} in the Raman spectrum results from the non-planar bending vibrations of this bond. Comparison of the band frequencies for polyglycine and *N*-MAA in the low-frequency region shows that the vibrations of the hydrogen bond give the bands of the same frequencies. These are the bands at 130 and 90 cm^{-1} for crystalline *N*-MAA³³ and 133 and 82 cm^{-1} for solid polyglycine. This gives reason to suppose that the hydrogen bond in the amide structures is characterised by the same vibrational frequencies regardless of the size of the molecule.

There is a discrepancy in the interpretation of the bands observed in this spectral region proposed by different authors. Itoh³³ and Nielsen²² assign the bands at 130 and 90 cm^{-1} observed for *N*-MAA to the bending and stretching modes of the hydrogen bridge, respectively, whereas Fanconi⁶⁷ interprets the band at 133 cm^{-1} for polyglycine as a stretching and that at 82 cm^{-1} as a bending vibration. These conclusions were made on the basis of theoretical calculations and seem to call for further consideration.

A number of publications^{68–74} are devoted to the studies of low-frequency spectra of the simplest chiral polypeptide, poly-L-alanine, the molecules of which also exist in two forms, *viz.* as the α -helix and the planar form. Normal coordinate analysis has been performed for both forms over all the spectral intervals (including

Table 6. Experimental and calculated frequencies for polyglycine-1 $(-\text{NH}-\text{C}^1\text{H}_2-\text{C}^2\text{O}-)_n$.⁶⁷

Frequencies / cm^{-1}		Assignment, potential energy distribution (%)
experiment	calculation	
296 K	120 K	
599 (Raman)	599 (Raman)	$623 (\tilde{E}_3)$ $\gamma(\text{C}^2\text{O})$ (43), $\delta(\text{C}^1\text{C}^2)$ (25)
587 (Raman)		$572 (\tilde{A}, \tilde{E}_1)$ $\nu(\text{C}^1\text{C}^2)$ (12), $\delta(\text{C}^2\text{O})$ (26), $\gamma(\text{C}^2\text{O})$ (49)
327 (Raman)	328 (Raman)	$319 (\tilde{A})$ $\delta(\text{C}^1\text{C}^2\text{N})$ (48), $\delta(\text{NC}^1\text{C}^2)$ (15), $\nu(\text{NC}^1)$ (12)
320 (IR)		$329 (\tilde{E}_1)$ $\delta(\text{C}^1\text{C}^2\text{N})$ (48), $\delta(\text{NC}^1\text{C}^2)$ (15), $\nu(\text{NC}^1)$ (12)
285 (IR)		$264 (\tilde{E}_3)$, $267 (\tilde{E}_2)$ $\delta(\text{C}^2\text{NC}^1)$ (41), $\delta(\text{C}^2\text{O})$ (31)
260 (Raman)	260 (Raman)	$257 (\tilde{E}_1)$ $\delta(\text{C}^2\text{NC}^1)$ (54), $\nu(\text{O}\dots\text{H})$ (21)
215 (IR)		$207 (\tilde{E}_1)$ $\delta(\text{C}^2\text{NC}^1)$ (43)
211 (Raman)	214 (Raman)	$201 (\tilde{A})$ $\delta(\text{C}^2\text{NC}^1)$ (21), $\delta(\text{C}^1\text{C}^2\text{N})$ (11), $\gamma(\text{NH})$ (30)
170 (Raman)	175 (Raman)	
133 (IR)		$149 (\tilde{E}_3)$ $\nu(\text{H}\dots\text{O})$ (92)
		$137 (\tilde{E}_1)$ $\delta(\text{NC}^1\text{C}^2)$ (27), $\tau(\text{C}^1\text{C}^2)$ (10), $\tau(\text{C}^2\text{N})$ (13)
		$131 (\tilde{A})$ $\delta(\text{NC}^1\text{C}^2)$ (33), $\tau(\text{C}^1\text{C}^2)$ (11), $\nu(\text{O}\dots\text{H})$ (11)
111 (Raman)	114 (Raman)	$106 (B_3)$ $\gamma(\text{NH})$ (22), $\tau(\text{C}^2\text{N})$ (21), $\tau(\text{C}^1\text{C}^2)$ (20)
82 (Raman)	87 (Raman)	$75 (B_1)$ $\gamma(\text{NH}\dots\text{O})$ (36), $\gamma(\text{C}^2=\text{O}\dots\text{H})$ (18), $\delta(\text{NH}\dots\text{O})$ (17)
		$69 (B_2)$ $\tau(\text{C}^1\text{C}^2)$ (30), $\tau(\text{C}^1\text{N})$ (29), $\gamma(\text{NH}\dots\text{O})$ (18), $\tau(\text{C}^2\text{N})$ (11), $\gamma(\text{NH})$ (13)

the low-frequency region).^{75–77} On the whole, the theoretical and experimental data were in satisfactory agreement.

Itoh *et al.*^{78–80} studied the FIR spectra for a series of poly-(α -amino acids) having helical and planar conformations of the chain and showed that each conformation has its own set of frequencies in the low-frequency region. In particular, it was shown^{69,70} for a series of polypeptides that the 'Amide V' band has a frequency about 610 cm^{-1} for compounds in the α -form, that for compounds in the β -form is in the region of 700 cm^{-1} , and a diffused band at 650 cm^{-1} corresponds to the disordered form. Itoh *et al.*^{78–80} examined the low-frequency spectra of a series of poly-(α -amino acids) and showed that the FIR region allows one to analyse the chemical and conformational composition of these homopolymers and copolymers of different amino acids.

It should be noted that Krimm and coworkers made a significant contribution to theoretical analysis of vibrational spectra of polypeptides. They have published a great number of papers including a series of papers having the common title 'Vibrational analysis of peptides, polypeptides and proteins' (*ca.* 40 publications). Thus the first publication of this series dates back to 1976,⁸¹ and one of the recent papers dates back to 1988.⁸² Krimm *et al.* have shown that normal coordinate analysis provides a rather full understanding of vibrational spectra of polypeptides and of a series of proteins having secondary structures such as α -helix, and β -layers. Normal coordinate analysis has been performed over the whole frequency interval up to lowest frequencies and in various approximations: for isolated molecules, with and without regard to hydrogen bonds, and for crystals. The value of this work is also in the fact that the force field established allowed one to perform calculations of the spectra of various conformations for both polypeptides and simplest proteins.

Recently low-frequency modes of polypeptides and proteins have attracted attention of researchers. The authors of

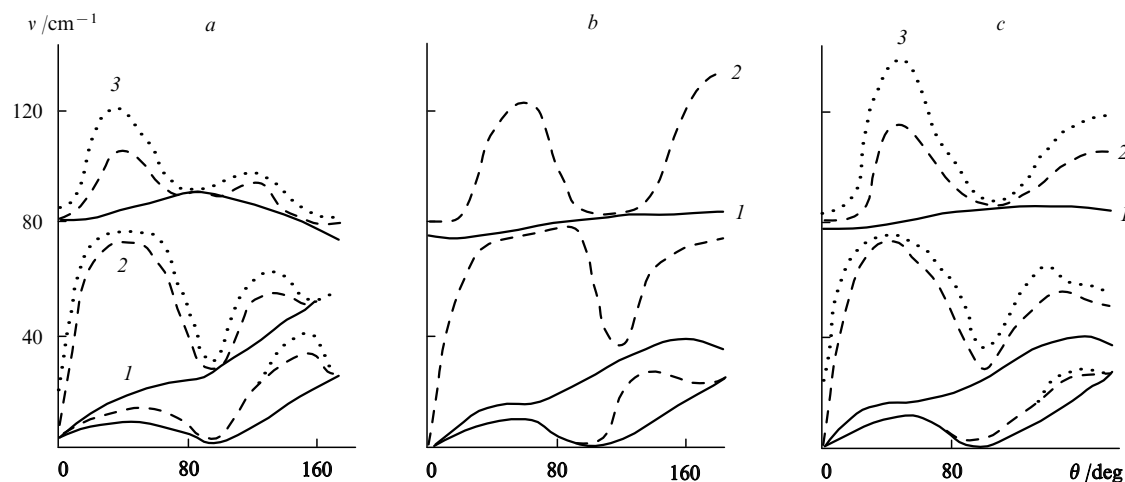


Figure 6. The low-frequency phonon-dispersion curves for the seven-masses model (a), one-mass model (b), and two-masses model (c) of poly-L-alanine in the form of the α -helix calculated for three values of the force constants: $F(\text{NH}\cdots\text{O}) = 0$ (1), $F(\text{NH}\cdots\text{O}) = 0.15 \times 10^{-3}$ (2), and $F(\text{NH}\cdots\text{O}) = 0.3 \times 10^{-3}$ dyne $\text{\AA}^{-1}$ (3).⁹⁰

Refs 83–85 believe that these modes play a definite role in biological processes. In particular, vibrations of the α -helix belong to these modes. ‘Breathing’ and acoustic longitudinal (of the type of ‘stretching accordion’) and transverse vibrations are the most interesting among them.

Itoh *et al.*⁷² and Fanconi *et al.*⁸⁶ were the first to calculate the frequencies of vibration of the α -helix for poly-L-alanine. The former authors considered a simplified model of the helix, in which the CH_3 group was considered as a single mass and the presence of the stabilising hydrogen bonds was taken into account. Normal coordinate analysis showed that the frequencies of 690, 370, and 260 cm^{-1} and in the region of 40–140 cm^{-1} correspond to helix deformations. The band in the range of 260 cm^{-1} was assigned to the ‘breathing’ mode, which was later confirmed by the Raman spectra.⁸⁷ The force was developed that allowed one to interpret the optically active modes of the α -helix, to calculate the frequencies of the modes with various phase difference and to obtain dispersion curves. Using these curves, which reflect the density of vibrational states, the INS spectra of poly-L-alanine were interpreted.⁸⁶ The vibrational frequencies appear to depend on the phase difference in the region below 1000 cm^{-1} , this dependence being especially pronounced in the region below 200 cm^{-1} where two acoustic modes are observed. These modes are strongly affected by hydrogen bonds.

The calculations show that in the case of the α -helix with a finite number of elementary units, the bands reflecting the helix length appear in the spectrum. Thus the frequency of the mode of the type ‘stretching of the accordion’ is inversely proportional to the helix length (n is the number of repeating units).

n	10	15	20	25	30	40	50	75	100
ν / cm^{-1}	67	50	40	32	28	24	20	15	11

Hence, the helix length can be estimated from longitudinal acoustic modes that manifest themselves in the Raman spectra. This method has found wide application in the studies of simple synthetic polymers such as polyethylene, polyoxymethylene, *etc.*^{88,89} In particular, the method permits the determination of the thickness of lamellas formed in polymers under various conditions. Using experimental data on longitudinal acoustic modes observed, the Young’s modulus of the helix can be easily calculated, which, for instance, is $E = 2.31 \times 10^{11}$ dyne cm^{-2} for poly-L-alanine.⁷²

The calculation of low-frequency modes for helices of more complex polypeptides becomes cumbersome due to the great number of atoms. In this case, simplified models can be used. Fanconi and Peticolas^{90,91} considered three simplified models of α -helix with poly-L-alanine as an example in order to calculate the

lowest-frequency modes. The first model is a seven-masses model including all the atoms of the elementary unit in which only the CH_3 group is considered as a single mass. This model is the closest to the structure of the real molecule. The second model is a one-mass model in which a repeating unit is considered as a single point mass. The third model is a two-masses model in which a chemical repeating unit devoid of the mass of the amide oxygen, is taken for one mass (this mass is located at the place of the oxygen atom in the α -helix), and the mass of the hydrogen atom located in its real position is taken for the other mass. In all the three models, the hydrogen bond is considered as a bond between the amide hydrogen and the third nearest oxygen atom thus allowing the helix structure to be reproduced.

Dispersion curves were calculated for three values of force constants of the hydrogen bond, namely, 0.3×10^{-3} dyne $\text{\AA}^{-1}$ (this force constant was taken from the force field for formic acid), 0.15×10^{-3} dyne $\text{\AA}^{-1}$ (the force constant was taken from the force field for *N*-MAA), and 0 dyne $\text{\AA}^{-1}$. The comparison of two dispersion curves obtained on the basis of these models and corresponding to the lowest-frequency modes shows (Fig. 6) that they are in good agreement with one another, the seven-masses model fits the two-masses model the best. Therefore, the lowest-frequency modes for helical structures can be calculated on the basis of a simple model that takes into account only intramolecular hydrogen bond. There is reason to suppose that this approach can be useful for the analysis of low-frequency modes of proteins.

VI. Proteins

Investigation of proteins by means of IR spectroscopy is a difficult task, for proteins have much more complex structures than synthetic polymers and polypeptides. Investigation of proteins is usually based on the analysis of the amide bands that provide information on the conformation of the backbone and side chains, on hydrogen bonding, *etc.*^{92,93} As a rule, the low-frequency region remains beyond the authors’ attention.

Buontempo *et al.*^{94,95} were among the first to study the FIR spectra of proteins. They have analysed the possibility of gaining structural information from the low-frequency modes. The authors found the presence of a wide intense absorption band centred near 150 cm^{-1} in all the FIR spectra for a series of globular proteins. Changes in the protein conformations and denaturation influence insignificantly the spectral pattern. No fine structure of the spectra in this region could be detected neither by increasing the resolution of the instrument nor by lowering the temperature of the sample. The authors supposed that the band broadening observed in the spectra of proteins originated from a

superposition of many bands corresponding to individual oscillators that have different force constants and effective masses. Since the proteins that differ significantly in the structure have practically the same spectra, the authors^{94,95} believe that the nature of this broad absorption can be rationalised by the anharmonic interaction between weak vibrations *via*, in the first turn, the H-bonded groups.

Chirgadze and Ovsepjan^{96,97} have performed more detailed investigations and have found that FIR spectroscopy can be useful for studies of conformational changes in, and denaturation of, proteins. The spectra of myoglobin reported in these papers and in Ref. 95 exhibit a broad absorption but with a rather pronounced fine structure (Fig. 7). It is seen from Fig. 7 that the bands at 376, 417, 422, and 470 cm^{-1} for natural myoglobin disappear upon denaturation of the protein in the alkaline medium, and the spectral pattern in the region below 300 cm^{-1} changes. Using the data on polypeptides with the structure of the α -helix and bearing in mind that 77% of the amino acidic residues are included in such a helix in the myoglobin under study, the authors associate the bands disappearing upon denaturation with the helical fragments of the protein molecule and propose the assignment for these bands. The changes in the bands at 324, 422, and 470 cm^{-1} reflect the changes in conformations of both the backbone and side chains. The authors obtained sufficiently good differential spectra by subtracting the spectrum of the natural protein from that of the denatured myoglobin. These spectra, however, should be regarded with due caution because false bands may result from subtraction, which have no physical meaning. These investigations⁹⁶ have led to the conclusion that FIR

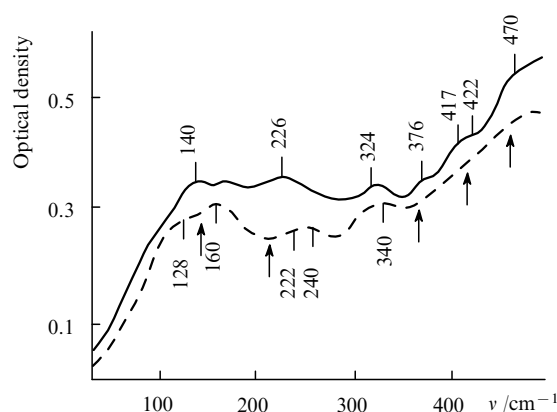


Figure 7. The IR spectrum of myoglobin in the natural (continuous line) and denatured states (dotted line). Arrows point to the changes in the spectra after denaturation.⁹⁷

spectroscopy provides definite information even for such complex molecules as globular proteins.

Other authors make the same conclusion (see, for example,^{98,99}). Ataka *et al.*⁹⁹ showed that the quality of the FIR spectrum depends significantly on the method of sample preparation. He proposed to study proteins in the form of monocrystals, which made possible a decrease in the surface scattering and to obtain the material with a dense packing. In this case, the spectrum consisted of a number of pronounced absorption bands that were absent in the spectrum of the sample prepared as a powder.

The interpretation of some bands in the low-frequency region in the IR and Raman spectra for crystalline lysozyme has been carried out empirically⁷² by comparing the spectra with the data on homopolypeptides and the above-considered myoglobin. The band assignment for lysozyme is, on the whole, close to that for myoglobin.⁹⁷ The authors supposed on the basis of the data of Ref. 72 that the bands at 56 and 25 cm^{-1} are associated with

longitudinal acoustic modes of the finite chains in the α -helix having five and fifteen amino acid residues, respectively.

There is a quite definite regularity observed in the FIR region when passing from low-molecular-weight biological compounds to complex high-molecular structures. If the spectra of the former (for example, of amino acids) have a distinct structure, the spectra of the latter (for example, of proteins) contain a broad diffuse band having some fine structure (note that this picture is not observed on going from amino acids to polypeptides). The same trend is noticed for nucleic acid compounds.¹⁰⁰ The spectra of nucleosides in the low-frequency region are clear-cut, they contain well-resolved, rather intense bands, whereas the spectra of nucleotides, polynucleotides, and nucleic acids are composed of broad bands with indistinct peaks, as in the case of proteins.

The nature of broad background absorption observed in the FIR spectra of various proteins has been discussed in the papers mentioned above. Buontempo⁹⁵ believes that this absorption can be related to anharmonic interactions between low-frequency modes. According to Chirgadze,⁹⁷ at least a part of this absorption results from a wing of the broad 'Amide V' band. However, Ataka *et al.*⁹⁹ believe that the broad background in the low-frequency region originates from the absorption of water molecules present in proteins, which seems to be the closest to the truth. This follows from the comparison of the shape of absorption bands in the spectra of ice and normal water with that of crystalline lysozyme at liquid nitrogen temperature and at room temperature, respectively. In general, it should be noticed that the existence of the broad background absorption in the spectra of proteins makes it difficult to investigate their FIR spectra.

Direct normal coordinate analysis becomes difficult, if at all possible. It is connected with the fact that the secular equation for molecules containing a large number of atoms and devoid therefore of symmetry, has a very high order and its solution becomes problematic even for modern computers. However, in some cases calculations can be successfully used. Thus frequencies have been calculated¹⁰¹ for β -coils that are difficult to identify in models, but occur in globular proteins together with the α -helices and planar β -structures.

The above-mentioned simplified methods for normal coordinate analysis of the α -helix developed for polypeptides⁹⁰ have been applied to the interpretation of low-frequency modes for one of the fragments of the α -helix in the pig insulin molecule.¹⁰² The authors regarded various peptide residues as single masses. In this case, they dealt with a secular equation of the 60th order.

Raman spectroscopy is an efficient experimental tool for the studies of proteins in the region below 100 cm^{-1} . The examination of Raman spectra provides information on vibrations at very low frequencies, up to 20 cm^{-1} , *i.e.* in the region that is difficult to study by FIR spectroscopy. As was already mentioned, the water molecules present in proteins give undesirable anisotropic scattering in the frequency region of 50 cm^{-1} and below. Nevertheless, the necessary signal can be detected by both experimental expedients¹⁰³ and computer processing of the spectra.¹⁰⁴ In this way it became possible to approach the excitation line. Thus bands were observed^{103–108} in the region of 20–40 cm^{-1} in the Raman spectra of a series of crystalline proteins, bands that disappear on dissolution of the protein in water. This behaviour of the bands can be explained either by their intermolecular nature or by the fact that these bands belong to the internal vibrations, which are rapidly damped out in the presence of water molecules.

An active interest in vibrations at these frequencies is observed. These modes are believed to be potentially sensitive to the order and to play a key role in the biological functions of macromolecules. Thus the vibrations of subunits, or molecules as a whole, is supposed to determine the activity of immunoglobulin.

There are a number of approaches to the description of these vibrations. Several models have been developed in order to estimate their frequencies. A model has been proposed¹⁰⁹ in which two parts of the protein globule move relative to one

another, the presence of water damping these vibrations. The model proposed by Go¹¹⁰ considers the protein molecule as a homogeneous elastic conglomerate, which is physically justified since in the case of low-frequency modes, the wavelength is large relative to the size of side pendants in the protein molecule. To estimate the frequencies of vibrational modes, the sample of protein was considered as a system of cubes arranged in space in a regular manner. This permitted the usage of boundary conditions and the consideration of an aggregate of elastic waves in this model system. Estimations have shown that the region of vibrational frequencies in this case is limited to an interval of 18–200 cm⁻¹.

Chou^{111–114} has developed a theory of vibrations in a quasi-continuous model that allows one to calculate the so-called 'dominating low-frequency modes' for various biomacromolecules. These modes, usually termed 'breathing', correspond, in the author's opinion, to the line observed in the Raman spectra at the lowest frequency. They seem to have the maximum amplitudes and, from the biological point of view, can be considered as 'activating low-frequency modes', the existence of which will activate the biological function of the macromolecule. According to Chou's theory,¹¹³ the frequency of these modes depends on the masses of the chains under consideration, the number of their coils, the number of hydrogen bonds, and the force constants of the latter. The low-frequency modes have been studied¹¹⁴ for the immunoglobulin molecule, which is known to consist of 12 domains of light and heavy types. Considering the domains to be of three types, Chou assigned the bands at 28 and 36 cm⁻¹ observed in the Raman spectrum¹¹⁵ to the 'breathing' modes of different types of domain.

It should be noticed that in the studies of nucleic acids, the low-frequency modes of the types considered also attract interest, because these vibrations are associated with the destruction of helices and changes in hydrogen bonding in them. A series of investigations in this direction has been carried out.^{116–122} Hence, the investigation of the low-frequency modes for complex biological systems may now be spoken of as a new field in molecular biophysics.

VII. Urethanes

Polyurethanes are very important for industry, that is why they are being widely investigated by a variety of methods including IR spectroscopy.¹²³ The appearance of a great number of publications devoted to compounds of this class has been stimulated by the creation of segmented polyurethanes exhibiting a number of valuable physicochemical properties. The application of spectral methods to the investigation of hydrogen bonding, orientational behaviour of rigid and flexible segments in the deformation appeared to be rather fruitful. However, a somewhat paradoxical situation exists in the spectroscopy of polyurethanes. There is a large body of publications devoted to the IR spectra of polyurethanes in the middle spectral region, whereas the data on Raman (excluding Refs 124 and 125) and FIR spectra for polyurethanes are practically lacking in literature. Only recently, the FIR spectra of polyurethanes have been reported.^{126–128}

Partially crystalline polyurethane synthesised from diphenylmethyl diisocyanate and 2,4-toluylene diisocyanate has been studied.¹²⁶ The absorption bands at 101 cm⁻¹ for the amorphous sample and at 107 cm⁻¹ for the highly oriented sample were assigned to vibrations of the hydrogen bond. These bands are temperature-sensitive (Fig. 8), and the spectra of oriented samples exhibit perpendicular dichroism. As is seen in Fig. 8, in the spectrum of the highly oriented sample, the band at 107 cm⁻¹ shifts to 115 cm⁻¹ on cooling from room temperature to -75 °C. In the melt, this band has a frequency of 88 cm⁻¹. A large band width in the region of 100 cm⁻¹ in the spectrum of polyurethane is related to the existence of different hydrogen bonds.

In the spectrum of a solution of the polyurethane in DMF, bands at 98 and 87 cm⁻¹ are observed. The authors assign the

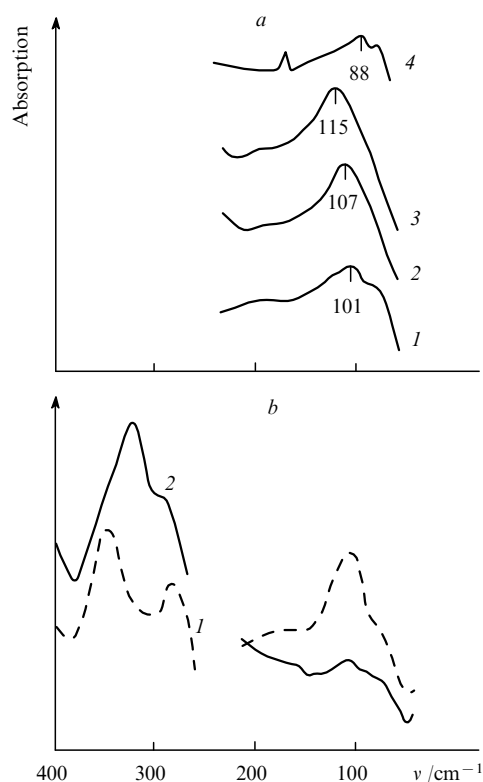


Figure 8. FIR (a) and polarised (b) spectra of partially crystalline polyurethane.¹²⁶

(a) The IR spectra of amorphous (1) and oriented (2) samples measured at room temperature. Curves 3 and 4 represent the spectra of the oriented sample measured at -75 and 180 °C, respectively; (b) polarised spectra of polyurethane extended by 300%: (1) the axis of polarisation is orthogonal to the axis of extension, (2) the axis of polarisation is parallel to the axis of extension.

former band to the inter-urethane hydrogen bonds and the latter to the bond between the urethane NH group and the carbonyl group in DMF. This choice of the solvent and concentration (30 mass %), is explained, probably, by the solubility of this polyurethane only in this solvent. However, DMF can form different types of hydrogen bonds with this compound and various self-associates. All this makes the band assignment rather ambiguous.

Analysis of the bands in the region of 270–400 cm⁻¹ was based on polarisation measurements for oriented samples. It is shown that the band at 320 cm⁻¹ exhibits the parallel dichroism and is sensitive to the packing of the molecules, which is seen from the changes in its intensity and half-width. This band almost disappears in the amorphous sample. By analogy with the data on polyesters,²¹ it is assigned to the coupled bending modes of the methyl and -O-CO-NH-C- groups, the main contribution to this mode being made by the bending vibrations of the methyl groups.

The bands exhibiting perpendicular dichroism are assigned to the torsional modes about the C-N bond (350 cm⁻¹) and to torsional vibrations of the CH₂ units (280 cm⁻¹) bound to the OCONH group. It might be expected that the frequency of the torsional vibration about the C-N bond should be affected by intermolecular interactions existing in the system, however, this band has the same frequency and intensity within a wide temperature interval for samples having different degrees of crystallinity, whereas the band at 100 cm⁻¹ undergoes significant changes. Unfortunately, the region of 200–270 cm⁻¹ in which, according to the literature data,^{21,45,46} these torsional modes are expected, is not covered by the interferometer used in Ref. 126.

Normal coordinate analyses for polyurethane molecules, which could be useful for a reliable assignment of the bands in the low-frequency region, are not yet available, which is why the interpretation of the bands presented in Ref. 126 has an empirical character.

Normal coordinate analysis has been performed for low-molecular-weight urethanes,^{124, 125} in particular, for urethane of the simplest structure, methyl *N*-methylcarbamate.¹²⁹ Vibrational analysis for 2,6- and 4,6-polyurethanes based on 1,6-hexamethylene diisocyanate and for a model urethane, dimethyl-1,6-hexamethylenedicarbamate, allowed only planar modes to be assigned.¹²⁵ Hence, there is no full assignment of the bands in the low-frequency region for the polyurethanes.

The absence of reliable data on normal coordinate analysis for compounds containing the urethane group and on the low-frequency region of vibrational spectra has stimulated thorough experimental studies of urethanes by FIR spectroscopy.

A series of low-molecular-weight model urethanes has been experimentally studied¹²⁷ in the FIR region. The comparison of a series of spectra for various crystalline polyurethanes synthesised on the basis of 1,6-hexamethylene diisocyanate and 2,4- and 2,6-toluylene diisocyanates allowed one to reveal a number of absorption regions in the interval of 70–400 cm⁻¹ typical of the vibrations of the urethane group, namely, 110–114, 140–170, 180–230, 270–290, 306–340, and 360–375 cm⁻¹. It was attempted to reveal the absorption bands associated with the intra- and intermolecular modes by means of temperature-dependent measurements. A decrease in temperature appeared to cause the most pronounced changes in the bands at 100–110 and 130–200 cm⁻¹, thus speaking for the assignment of these bands to the intermolecular modes (Fig. 9). A high-frequency shift of the former band, as in the case of crystalline amides, is insignificant (1–5 cm⁻¹). It is this band that is related to intrinsic vibrations of the hydrogen bond in amides³³ and in the above-considered polyurethane.¹²⁶ As for the region of 130–200 cm⁻¹, the most significant shift (15–25 cm⁻¹) as the temperature dropped to –140 °C was observed in the spectra of diurethanes synthesised from aliphatic diisocyanate. The 'Amide VII' band in which the torsional motion about the C–N bond makes the main contribution is known to lie in this region.^{33, 57, 129} The torsional mode of the urethane group neighbouring the flexible polymethylene chain is supposed to depend on the conformation of the latter and on the hydrogen bond formed in the crystal, thus leading to a temperature dependence of this band. It is also possible that in the

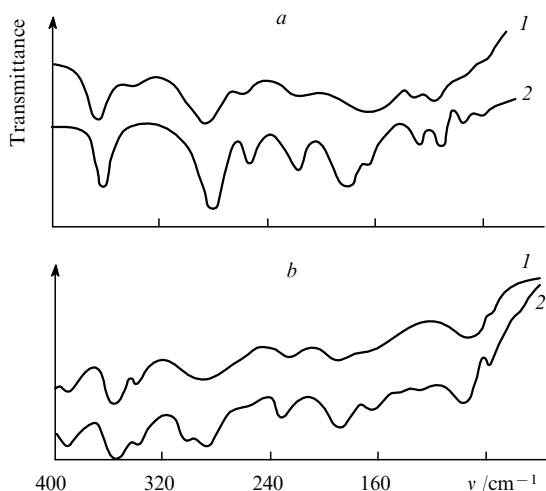


Figure 9. The IR spectra of diurethanes CH₃CONH(CH₂)₆NHC(=O)Bu (a) and CH₃CONHC₆H₄CH₂C₆H₄CONHCH₃ (b) in the region of 40–400 cm⁻¹ measured at 25 (1) and –140 °C (2).¹²⁷

case of aliphatic urethanes, the intrinsic vibration of the hydrogen bond contributes significantly to the absorption at this frequency.

In the spectra of urethanes containing the benzene ring, there is an absorption band at 350 cm⁻¹, which can be assigned to the vibrations of this group rather than to the torsional modes about the C–N bond.¹²⁶

Interurethane hydrogen bonds play a substantial role in the formation of associates in amorphous oligourethanes based on oligodivinyisoprene. The features of structure formation in these associates have been studied by IR spectroscopy.¹³⁰

The investigation of the FIR spectra for oligourethanes containing terminal and internal urethane groups has revealed an interesting feature.¹³¹ It was found that the spectral picture in the region of 60–250 cm⁻¹ is independent of the type of diisocyanate used in the synthesis, but is determined only by the arrangement of the urethane block. When the urethane fragments are terminal, association is facilitated for these compounds as compared to that for the compounds in which the urethane fragments are located inside the chain. In the latter case, the oligodivinyisoprene chains tend to block the urethane groups. Nevertheless, in this case, hydrogen bonds between the urethane groups are also formed. The data on the FIR spectra and on the bands of the NH– and C=O stretching vibrations indicate that not only the degree of association but also the system of hydrogen bonds are different for the oligomers with the terminal and internal positions of the urethane fragment, for the frequencies of the absorption bands of the bonded NH–, CO–, and NH...OC groups differ from one another.¹³¹ It might be supposed that the bands at 105 and 85 cm⁻¹ observed in the FIR spectra of oligourethanes with terminal and internal positions of the ure-

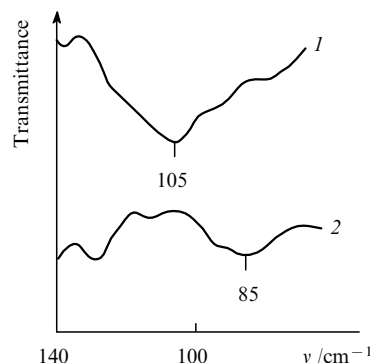


Figure 10. The IR spectra of urethane oligomers in the region of 60–140 cm⁻¹ with the terminal (1) and internal (2) arrangements of the urethane fragment.¹²⁸

thane groups, respectively, result from the vibrations of hydrogen bonds of various energies (Fig. 10).

Some polyurethanes have been studied by FIR spectroscopy.^{127, 128} Temperature and polarisation measurements have revealed the absorption bands in the ranges of 130–200 and 80–100 cm⁻¹ which are sensitive to the hydrogen bonds. As in the spectra of model diurethanes (see Fig. 9), two bands in the regions of 90 and 200 cm⁻¹ appeared to be temperature sensitive (Fig. 11). Both bands exhibit preferentially a perpendicular dichroism (Fig. 12). The results obtained allowed the authors to suppose that the band at 200 cm⁻¹ belongs to the torsional vibrations about the C–N bond and that at 90 cm⁻¹ is assigned to vibrations of the hydrogen bond formed between the urethane groups.

The FIR spectra of more complex cross-linked polymers^{127, 128} are very similar and independent of the nature of the diisocyanates used for the synthesis and of the concentration of cross-linkages in the polymer network. The authors of Ref. 131

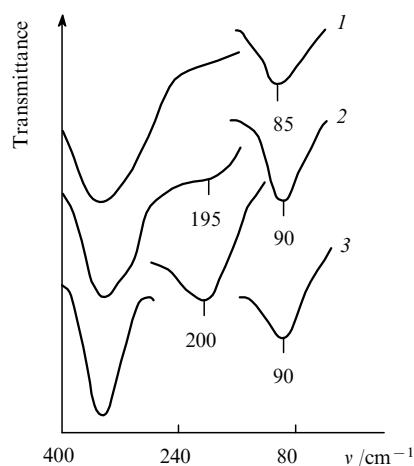


Figure 11. The IR spectra of polyurethane synthesised from polybutylene glycol adipate and diphenylmethane diisocyanate in the region of $60\text{--}400\text{ cm}^{-1}$ at 120 (1), 25 (2), and $-140\text{ }^{\circ}\text{C}$ (3).¹²⁸

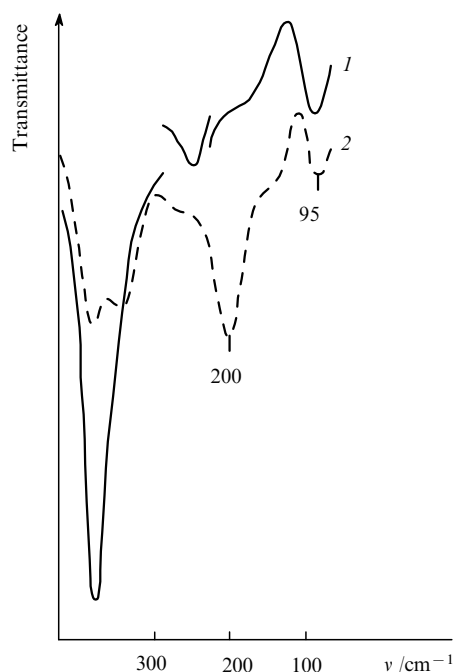


Figure 12. Polarised spectra of polyurethane synthesised from polybutylene glycol adipate and diphenylmethane diisocyanate extended by 350% .¹²⁸

(1) The polarisation vector is parallel to the axis of extension, (2) the polarisation vector is orthogonal to the axis of extension.

connect the presence of the band at 85 cm^{-1} with the vibrations of the hydrogen bond.

Hence, from the FIR spectroscopic studies of urethanes that have recently been started, the absorption band was found that corresponds to the vibration of the hydrogen bond in these systems. This is a new step in research on the structure of polyurethane systems.

VIII. Conclusion

The presented material shows that the application of low-frequency vibrational spectroscopy to the investigation of amides and urethanes, and in particular, of biological objects, extends the capabilities of the analysis of molecular vibrations. Thus, many tasks connected with the studies of intramolecular and intermo-

lecular vibrations can be successfully solved for low-molecular-weight and especially crystalline compounds. However, the application of low-frequency spectroscopy to the studies of such complex biological objects as proteins resulted in a modest success. In this case, the spectrum consists of broad diffused bands with weak separate peaks on the background of this band. The comparison of calculated and experimental spectra for simple proteins indicates that only a small part of the bands expected from calculations is observed in the experimental spectra. That is why the interpretation of the bands becomes problematic.

The use of low-frequency spectroscopy for the studies of relatively simple polymeric systems such as polyamides and polypeptides is undeniably successful. In many cases, it provides unique information. Certainly, only this method makes it possible to observe experimentally the bands of intermolecular vibrations including intrinsic vibrations of hydrogen bonds. The complex of techniques has been developed to assign experimentally the bands observed in the spectra to these modes. The technique of the $R(\nu)$ representation used in Raman spectroscopy provides a possibility to investigate hydrogen bonds in liquid amides.

The use of FIR spectroscopy in studies of conformational transformations in polyamides and polypeptides has shown its advantages over spectroscopy in the middle region, for the low-frequency region is especially sensitive to chain conformations. Low-frequency spectroscopy can be useful in studies of polymorphism in polymers and of the conformational composition of macromolecules both in the qualitative and quantitative aspects.

As a rule, IR spectroscopy is beneficial for investigations of polyamides and polypeptides in the low-frequency region, whereas the Raman spectra have been less studied. Therefore, investigations of Raman spectra in the region close to the excitation line are promising, because according to existing ideas the frequencies of longitudinal acoustic modes in helices of polypeptides, proteins, and nucleic acids as well as 'breathing' modes of globular systems are located in this region. The elucidation of the mechanism of these vibrations can provide a new tool for studies of vibrations of large molecular aggregates or macromolecules as a whole.

As far as the class of urethanes is concerned, it should be noticed that despite the obvious advantages of the low-frequency method, it has scarcely been used for studies of these objects. There is rather voluminous literature on the spectra of polyurethanes in the middle region. The role of the hydrogen bond and conformations of the molecules is very important for these compounds, that is why the examination of the low-frequency region of vibrational spectra is a very interesting and promising task for understanding the structure of the substance.

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Competitive coordination: ambident ligands in the modern chemistry of metal complexes

A D Garnovskii, D A Garnovskii, I S Vasil'chenko, A S Burlov, A P Sadimenko, I D Sadekov

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Abstract. Data on the problem of competitive coordination, obtained mainly during the last 10 years, are surveyed and treated systematically. The competitive binding of metals in complexes of bi- and poly-dentate ligand systems — simple diatomic and triatomic compounds (N_2 , O_2 , CO , CO_2 , CS_2 , *etc.*), ambident anions (CN^- , NCX^- , NO_2^- , SO_3^{2-} , *etc.*), and neutral aliphatic, aromatic, and heterocyclic compounds, including chelating organic ligands — is examined. Attention is specially concentrated on non-traditional ways in which typical ligand systems are coordinated and on regioselective synthesis as a method for the specific synthesis of metal complexes with a specified location of the coordinate bond. The bibliography includes 575 references.

I. Introduction

Competitive coordination is the term applied to the ability of bidentate and polydentate ligands to react with metal atoms at different donor (nucleophilic) centres. Investigators encountered the problem of competitive coordination for the first time a quarter of a century ago.^{1,2} Review publications^{2–24} have been devoted to individual aspects of this problem. They include reviews on the coordination of nitrogen,^{4,7,8} oxygen,^{9,10} carbon monoxide,^{11–13} and carbon dioxide^{14,15} molecules. The interest in the problem under consideration can be accounted for by the fact that it embraces problems of donor–acceptor interaction,^{18,25,26} bond isomerism,^{3,5,6,17,18,27–32} and the synthesis of complexes of a particular type (stereoselective synthesis)^{4,22,31–34} and with a specified location of the coordinate bond (regioselective synthesis)^{17,22,33–35} and specific coordination of metals in biologically important systems.^{35–39}

In order to account for the different ways in which bidentate and polydentate ligands are coordinated, Pearson's principle of hard and soft acids and bases (HSAB) was applied.^{40–42} In relation to competitive coordination,² it is formulated as follows: in polydentate ligand systems, it is possible to identify hard

(mainly N and O) and soft (P, As, Sb; S, Se, Te; π , σ -donors) reaction centres, and the HSAB principle itself indicates in this instance² the preferential binding of hard Pearson acids (metal salts) to hard donor centres and of soft acids to soft nucleophilic atoms or π -donor groups of ligands.[†]

The concepts of the 'hardness' and 'softness' of acids and bases have been examined many times.^{2,3,18,25–27,40–42,45,46} The collective nature of these concepts, embracing characteristics of the reactants such as polarisability, electronegativity, and ion size, were emphasised in this connection.^{2,3,18} Nowadays attempts are being made to develop the quantitative aspects of the HSAB concept (see, for example, Pearson⁴⁵). Pearson's attempts⁴⁵ to estimate hardness and softness theoretically merit special attention. According to Pearson⁴⁵, the future developments of these studies will involve the establishment of the relation between the difference in the energies of the highest occupied and lowest unoccupied molecular orbitals and the hardness of the system. In a later study, Datta⁴⁶ emphasises that, although hardness is an important reactivity index and has been estimated quantitatively, a full theoretical justification of the HSAB principle, *i.e.* the principle that 'hard likes hard' and 'soft likes soft', has not yet been achieved. In a study of the thermodynamics of exchange reactions of the type



with participation of lithium hydrides and halides, hydrogen halides, monohalo-derivatives of methane and silane, and other reagents,⁴⁶ he concluded that the formation of the hardest of the possible compounds is the driving force of the exchange reaction and that the average hardness of the products becomes greater than that of the initial compounds.

It is noteworthy that, although bidentate and polydentate ligand systems with soft and hard donor centres include a wide range of compounds, they do not embrace the entire series of ligands. Thus they do not include molecules which contain only hard or only soft nucleophilic centres and are capable of binding to the metal in different ways.

Evidently the HSAB approach reduces the number of ligand systems which could be considered within the framework of the problem of the competitive coordination of bidentate and polydentate ligands.

In the present review, we tried to examine all the possible ways in which the coordinate bond can be located in complexes with the

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[†] The possibility of employing the HSAB concept to explain the different ways in which ligands are bound to metals in complexes was first demonstrated in relation to complexes of pseudohalide anions.^{43,44}

most familiar ligands — both with simple inorganic molecules and with complicated organic compounds having several donor atoms and groups. Attention is concentrated on the nontraditional ways in which typical ligands are coordinated and on regioselective synthesis. Mainly the literature of the last 10 years has been used in the review.

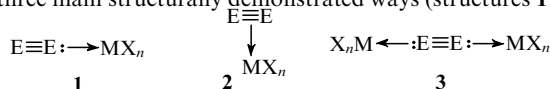
II. Types of competitively reacting ligands

For a correct understanding and assessment of the regioselectivity of complex formation reactions, it is necessary to consider only thermodynamically stable products (complexes) formed under the conditions of kinetic control.^{3, 47} In other words, one is dealing with the thermodynamic stability of the products of the initial attack by the metal (complex-forming agent) on the nucleophilic centre of the ligand. This postulate is extremely significant, since in many cases complexes in which the ligands are prone to tautomerism undergo various metallotropic processes.^{48–56} The latter are frequently accompanied by a change in the centre where the coordinate bond is located in relation to the expected location.

Ligand systems forming bond isomers comprise bidentate and polydentate and homogeneous and heterogeneous inorganic compounds, ambident[‡] anions,¹ and diverse organic compounds.

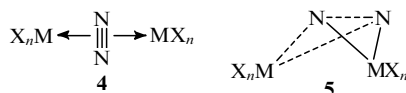
1. Inorganic molecules

The homoatomic nitrogen,^{4, 8, 57–66} phosphorus,^{67–69} and arsenic^{69, 70} molecules in coordination compounds of metals function as monodentate or bidentate ligands and are coordinated in three main structurally demonstrated ways (structures 1–3).

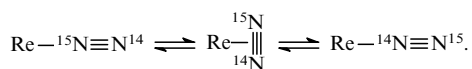


E = N, P, As.

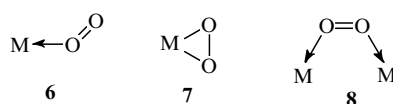
Apart from the structures indicated, complexes described by formulae 4,^{8, 71} and 5⁸ (see also the footnote below⁸) have been noted.



The bond isomers of the nitrogen complexes 1 and 2 may be in equilibrium. Thus exchange described by the following equilibrium reaction has been detected for the compound $[(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_2\text{N}_2]$ by ¹⁵N NMR.⁶²

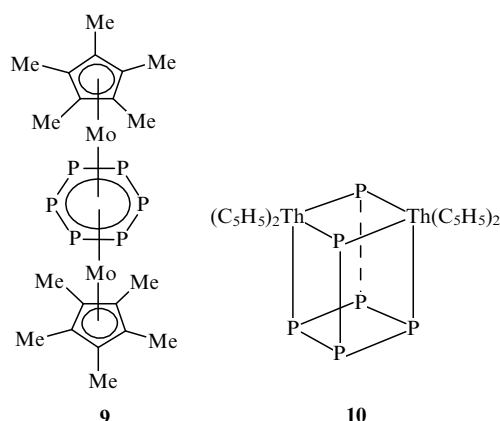


Bond isomers similar to complexes 1–3 are characteristic also of the complexes formed by diatomic oxygen (structures 6–8),^{9, 10, 72} sulfur,^{73–75} selenium,^{76, 77} and tellurium^{77–82} molecules.



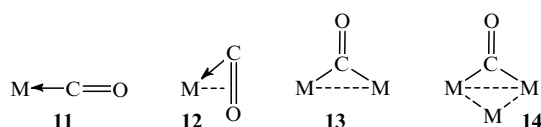
Among inorganic homoelement ligands, compounds containing three and more atoms are encountered. This is particularly characteristic of phosphorus, for which metal complexes based on trimeric,⁸² tetrameric,⁸³ pentameric,⁸⁴ and hexameric^{85–87} phosphorus-containing ligand systems with different locations of the coordinate bond have been obtained. It is striking that the P₆

molecule can behave not only as a η^6 -coordinated ligand (for example, in the triple-deck complex 9),⁷⁶ but also as a η^3, η^3 -binding ligand system (complex 10).⁸⁷



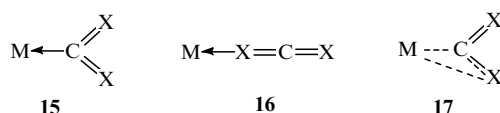
Different types of coordination of Se_n and Te_n molecules have been considered in a review.⁸²

The heteroelement diatomic CO,^{4, 11–13, 27, 28, 69, 88–90} CS,^{69, 91–93} and NO^{69, 94–96} molecules also behave as monodentate and bidentate ligands and can function as both terminal and bridging ligands. For example, the formation of the following structures has been demonstrated for carbon monoxide:

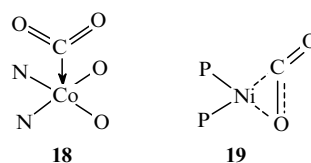


Similar types of coordination are characteristic of carbon monosulfide^{91–93} and nitrogen monoxide.^{94–96}

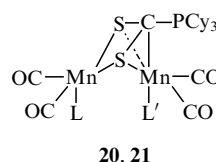
There are various types of coordination of heteroelement triatomic molecules: CO₂,^{14, 15, 69, 97} COS,¹⁵ CS₂,^{15, 98–100} and SO₂.^{5, 69, 101–105} The formation of three types of metal — ligand bonds (compounds 15–17) has been demonstrated^{15, 97} for carbon dioxide complexes with the aid of X-ray diffraction (XRD) data.



The type 15 (X = O) structure is characteristic of the cobalt complex 18,⁹⁷ while structure 17 (X = O) occurs in the nickel complex 19.¹⁵



Like CO₂, carbon disulfide is bound to the metal in different ways.¹⁵ For example, in the dinuclear complex $[\text{Mn}_2(\text{CO})_9(\text{CS}_2)\text{PPh}_3]$ ¹⁰⁰ the above ligand behaves as a S-monodentate species, while in the manganese complexes 20 and 21 (Cy = cyclohexyl) the same ligand system behaves as a C–S bridge.¹⁰⁰



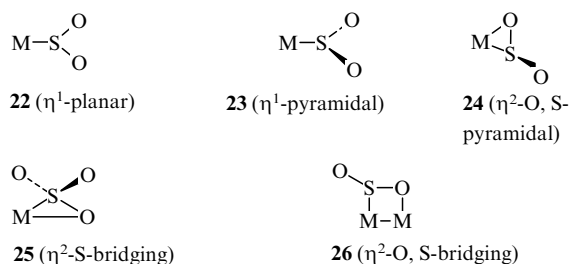
20: L = L' = CO;

21: L = L' = Ph₂PCH₂PPh₂.

[‡] Ambident systems are inorganic and organic molecules and ions with conjugated donor atoms.

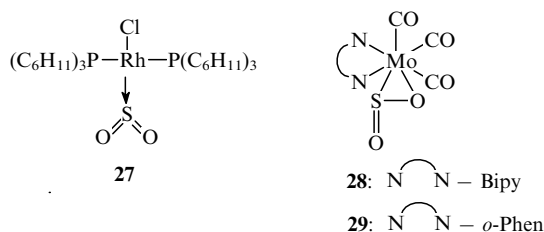
§ R J Deeth, S A Laytord *J. Chem. Soc., Dalton Trans.* 1 (1995); N Desmangles, H Jenkins, K B Rupp, S Gamborotta. *Inorg. Chim. Acta* **250** 1 (1996)

Five modes of coordination (compounds **22–26**) are characteristic of sulfur dioxide complexes,^{69, 101–105} two of the compounds (**22** and **23**) being stereoisomeric.



In particular, it has been demonstrated by X-ray diffraction¹⁰¹ that structure **27** with a cis-planar dioxide fragment (type **22**) occurs in the complex $[\text{RhCl}(\text{PCy}_3)_2(\eta^1\text{-SO}_2)]$.

The pyramidal O,S-binding of the SO_2 group is characteristic of the complexes $[\text{Mo}(\text{CO})_3(\text{Bipy})(\eta^2\text{-SO}_2)]$ and $[\text{Mo}(\text{CO})_3(o\text{-Phen})(\eta^2\text{-SO}_2)]$ with the same fragment (structures **28** and **29**, type **24**).

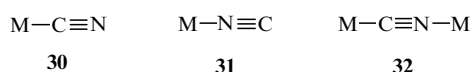


Bond isomers of metal complexes of heteroelement ligands, the molecules of which incorporate four (N_2S_2),¹⁰⁶ six (N_2S_4),¹⁰⁷ and eight (N_4S_4)¹⁰⁸ heteroatoms, have been described.

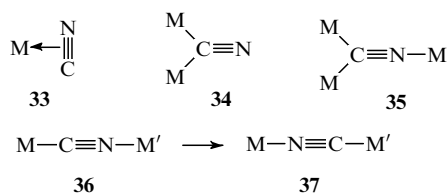
2. Ambident inorganic anions

Among ambident anions, the following have been most thoroughly investigated as competitively reacting ligands: cyanide^{5, 16, 27, 28, 109–113} nitrite,^{3, 5, 18, 27, 28, 114–119} sulfite,^{5, 18, 103, 117, 118, 120} and triatomic pseudohalides,^{2–5, 17, 18, 31, 32, 43, 44, 121–125}

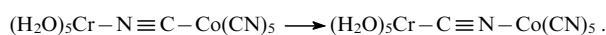
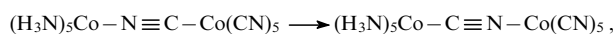
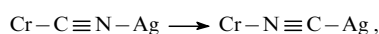
The formation of structures of three types (**30–32**) has been demonstrated for the cyanide anion.^{5, 16, 27, 112}



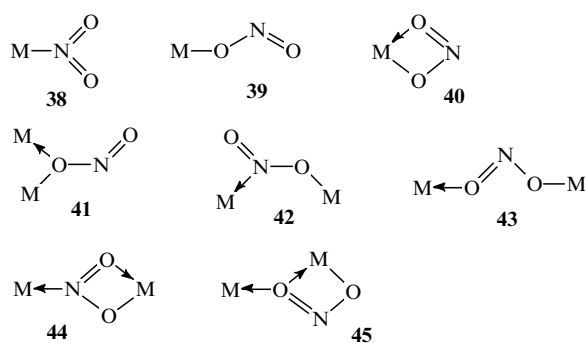
In addition, the coordination types **33–37** are possible^{16, 27} (the last two types of coordination correspond to the two stereoisomers **36** and **37**).



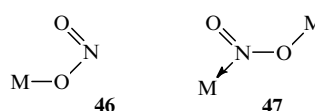
The above C,N-isomerisation has been observed in the following bimetallic complexes: Cr, Ag; Co, Co; Cr, Co.



Eight types of bond isomers (**38–45**) have been proposed for complexes of nitrite anions.^{5, 27, 114, 119}

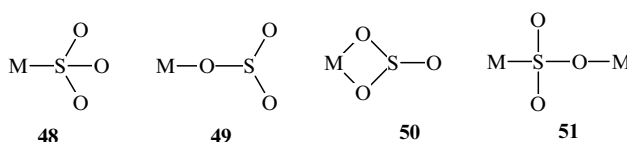


The stereoisomers of anionic metal nitrite complexes have also been described:⁵ angular (**46**) and *trans*-planar (**47**).



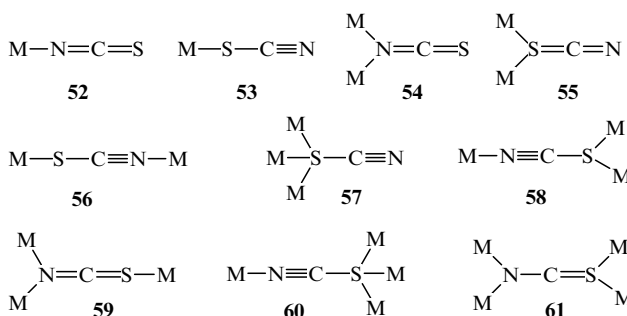
Numerous specific examples of nitrite complexes have been presented in a review.⁵

The complexes of the sulfite anion are represented by bond isomers in which the SO_3^{2-} fragment behaves as S- (**48**),^{2, 3, 5, 103, 118} O- (**49**),^{5, 18, 103} and O,O-chelate (**50**)^{5, 103} ligands or an O,S-bridging ligand (**51**).^{103, 117, 118}



Other variants of coordination have also been put forward for dinuclear and polynuclear complexes of the SO_3^{2-} anion.¹⁰³ In the majority of these complexes the location of the coordinate bond has been established from vibrational spectroscopic data and the results of kinetic studies.^{5, 103} Definite progress has been achieved in the study of the structures of sulfite complexes by NMR spectroscopy involving different nuclei.^{117, 118, 125, 126} It has been established by X-ray diffraction^{118, 125} that the three cobalt atoms in the trinuclear anion of the complex $\text{Na}_4[\text{Co}_3(\text{NH}_3)_6(\text{SO}_3)_6]$ are linked by the bridging SO_3 group. The SO_3 groups are bound to two cobalt atoms via sulfur atoms and to the third cobalt atom *via* an oxygen atom.^{118, 125} The metal atoms are coordinated *via* oxygen and chalcogen atoms in complexes of the selenite^{5, 118, 125} and tellurite^{118, 125} anions. On the other hand, the sulfate anion is usually bound to the metal atoms *via* an oxygen atom and performs mainly a bridging function.^{127–130}

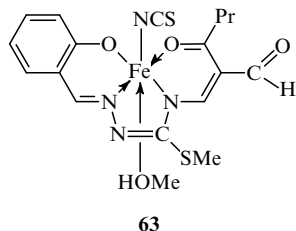
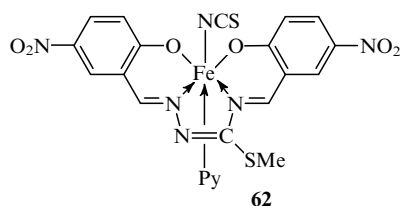
For complexes of pseudohalide anions (NCX , where $\text{X} = \text{O}, \text{S}, \text{or Se}$), the structures with ten modes of coordination (**52–61**) of the NCS anion as an example have been proposed.^{4, 5, 17, 18, 43, 44, 124}



Extensive compilations of X-ray diffraction data for different modes of coordination of NCX anions are available in monographs^{17, 44} and reviews.^{5, 124} The greatest number of complexes contain the $\text{M}-\text{N}=\text{C}=\text{X}$ fragment (**52**). This type of coordina-

tion is characteristic of, for example, gallium,¹³¹ indium,¹³² tin,^{133, 134} iron,^{135–137} cobalt,^{138, 139} manganese,^{140, 141} nickel,^{142, 143} and copper^{144–149} complexes.

An analogous M–NCS coordination has been observed also in chelate complexes, for example complexes **62**¹⁵⁰ and **63**.¹⁵¹



The Fe–NCS coordination in the adducts **62** and **63** was demonstrated by X-ray diffraction. The number of structures of the pseudohalide complexes in which the M–X–C≡N coordination (**53**) occurs is significantly smaller. Such structures are observed mainly in complexes of soft metals.^{2–5, 17, 18, 43, 44, 124, 152, 153} It is striking that there are virtually no descriptions of structures with a pure M–SCN bond in the literature of recent years, although in certain cases (see, for example, Maurya *et al.*,¹⁵⁴) its occurrence has been postulated.

Complexes with a bridging M–NCS–M' bond occupy an important place among the coordination compounds of pseudohalides. Early information about such structures is available in reviews^{5, 34, 44, 122, 124, 152} and monographs.^{4, 17, 18} Among the studies in recent years, we shall mention those devoted to the structures of bismuth(III),¹⁵⁵ antimony(III),¹⁵⁶ molybdenum(IV),¹⁵⁷ nickel(II),^{158, 159} copper,^{160, 161} and ruthenium(IV)¹⁶² pseudohalide complexes as well as the heterodinuclear lanthanum–mercury complex.¹⁶³ Soft–hard Hg–SCN bonding and hard–hard La–CNS bonding are observed in the La–Hg complex. The latter type of bonding is characteristic also of the mononuclear lanthanum thiocyanate compound La(NCS)₃·2(Me₂N)₃PO.¹⁶⁴

The structure of the complex AgLSCN·0.25L (L = α,α-bipyridyl),¹⁶⁵ in which the rarely encountered type **55** coordination occurs, is of undoubted interest.

The data presented above on the competitive reactions of pseudohalide ions refer mainly to soft–hard interactions,^{2, 3, 5, 18} i.e. they take into account the nature of the donor N,X atoms on the complex-forming metals. At the same time, one should bear in mind that the nature of other ligands and the conditions in the synthesis of the pseudohalide complex exert an extremely significant influence on the nature of the binding of NCX anions to metals. Extensive data, partly published in Refs 4, 17, 122, 124, 153, 165, and 166, have accumulated on these problems. Bond isomerism of the type MNCS⇌MSCN is quite frequently observed in complexes of this type.^{4, 123, 167}

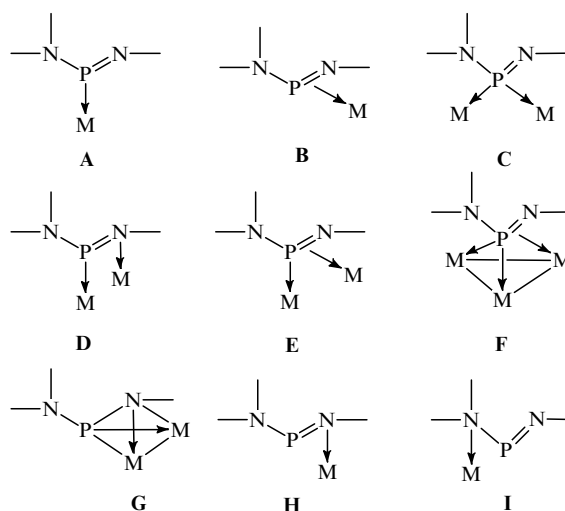
It is noteworthy that the results of a recent *ab initio* quantum-chemical calculation for pseudohalide ions¹⁶⁸ indicate the possibility of the chelation of the NCX groups. However, there are as yet no experimental data confirming this conclusion.

There are data on various modes of coordination of other ambident anions also: CNO[–] (see, for example, Refs 5 and 17), CNS[–],⁵ [C(CN)₃][–],¹⁷ NO₃[–],^{27, 28, 169, 170} NSO[–],^{5, 169} SNO[–],⁵ NSO₂[–],¹⁶⁹ S₂O₃^{2–},^{3, 5, 18, 103, 117, 118, 171} S₂CO₃^{2–},⁵ OSNH[–],⁵ and NS₃[–].¹⁶⁹

3. Organic bidentate and polydentate ligand systems with donor atoms — the elements of the main Group V and VI subgroups

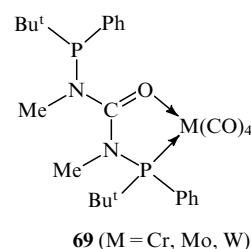
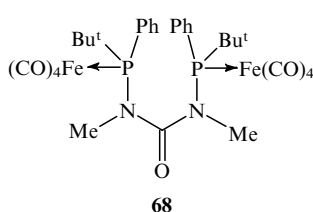
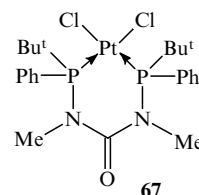
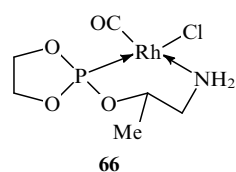
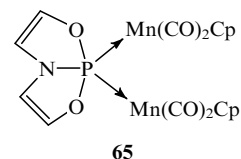
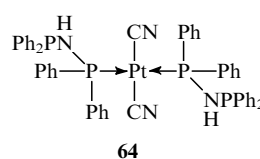
Extensive data on the competitive coordination of organic bidentate and polydentate ligands have been collected in reviews^{2, 3, 5, 6, 29, 30} and monographs.^{4, 17, 18, 25, 26} In the present review, the fundamental results in this field achieved in recent years will be considered.

Two reviews^{172, 173} contain compilations of data on ligands with N,P-donor atoms and the complexes obtained from them. It had been shown earlier that mainly the phosphorus atom participates in the coordinate bond formed in complexes of these ligands. However, when the disposition of the nucleophilic centres is favourable for the formation of a bridge or chelation, metalocyclic structures with participation of N and P atoms are obtained regardless of the hardness or softness of the metal salts. Thus the formation of at least seven types of transition metal complexes (**A–G**) is possible for the amides of the imidophosphonous acid R¹R²N–P=NR³.¹⁷²



The possible structures **H** and **I**, in which coordination is achieved *via* the nitrogen atom, were not considered in the above study¹⁷² for reasons which are not clear.

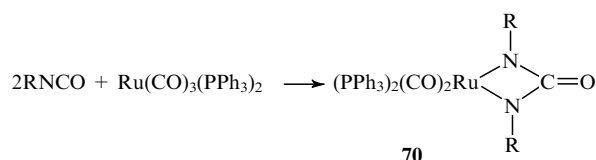
A similar situation is characteristic also of ligands containing a donor oxygen atom (compounds **65**,¹⁷⁵ **66**,^{176, 177} **67**, and **68**,^{173, 178}) apart from the N,P atoms (compound **64**¹⁷⁴).



An increase in the electron-donating activity of the carbonyl oxygen compared with the ester oxygen (structure **65**) and a disposition of the donor centres suitable for chelation lead to the chelate structure **69**.¹⁷⁸

Phosphazenes, the coordination chemistry of which involves a series of complexes with hard (N) and soft (P) coordination, are N,P-donor ligands.^{18, 179} Several examples of complexes obtained from N,As(Sb)-containing ligands are known,^{18, 175} but these do not allow a discussion of the characteristic features of their competitive reactions.

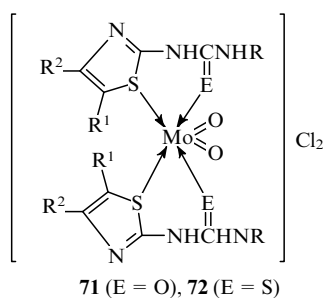
There are comparatively few new data on the competitive coordination of N,O-donors. The study of the structures of the complexes SnCl_4 and EtSnCl_3 with tetramethylurea confirmed² that the latter is a predominantly monodentate O-donor ligand.^{180, 181} Thus an O–Sn bond is formed in the complex between 1,3-dimethylurea and SnCl_4 . This conclusion was reached on the basis of IR and Mössbauer spectroscopic data.¹⁸¹ We may note that reliable information about the possibility of the involvement of the urea nitrogen atoms in coordination is lacking in the studies published previously. Complexes with N-coordinated urea **70**, obtained as a result of the reaction¹⁸²



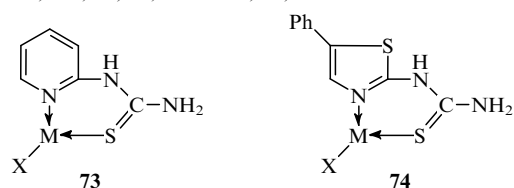
are therefore of undoubted interest.

The coordination chemistry of organopseudohalides of the type RNCX ($\text{X} = \text{O}, \text{S}, \text{Se}, \text{Te}$) has been examined in a review.¹⁸² It is remarkable that the interaction of ligands of this type with metal salts and carbonyls is accompanied not only by the formation of the adducts $(\text{RNCX})_m \cdot \text{RX}_n$ but also by chemical reactions of the ligand systems.¹⁸²

Among the ligands containing N- and S-donor centres, thiourea (L) and its derivatives are widely represented. Thus complexes between thiourea and ruthenium(III) trifluorosulfonate¹⁸³ and copper(II) bis(dimethylglyoximate),¹⁸⁴ between 1,3-dimethylurea and tin chloride,¹⁸¹ between 1,3-diphenylurea and rhodium(I) chloride,¹⁸⁵ and between ethylenethiourea and copper(I) sulfate¹⁸⁶ have been obtained. It has been suggested that S–N coordination obtains in the chelate complexes **71**.^{187, 187} **72**,¹⁸⁷ **73**,¹⁸⁸ and **74**.¹⁸⁸



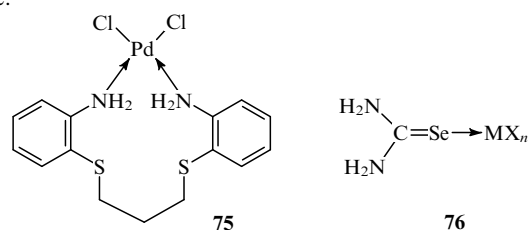
$\text{R} = \text{H}, \text{Alk}, \text{Ar}; \text{R}^1, \text{R}^2 = \text{Alk}, \text{Ar};$



$\text{M} = \text{Cu(I)}, \text{Ag(I)}; \text{X} = \text{Cl}, \text{Br}.$

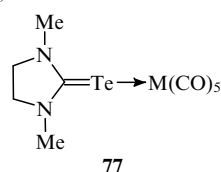
Whereas the occurrence of structures **73** and **74** is not open to serious objections, the possibility of the involvement of S and not N atoms of the thiazole ring (structures **71** and **72**) is hardly realistic.^{189, 190} The chelate structure **75** is believed probable for

the complex between a diaminodithioether and palladium chloride.¹⁹¹

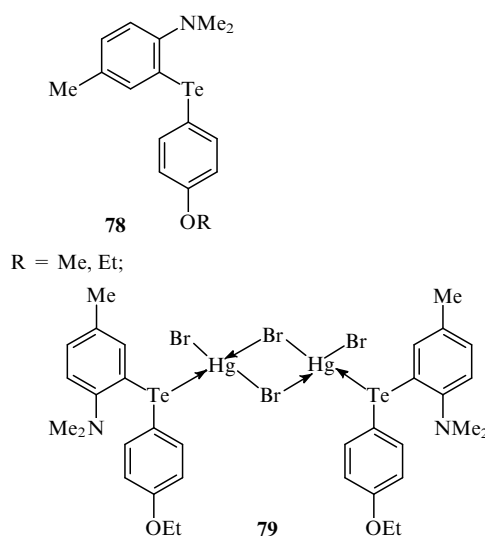


Coordination compounds of N,Se-containing ligands are mainly represented^{2, 18, 192–194} by selenourea complexes in which the Se–M bond is formed (compound **76**). In particular, such a bond has been found (on the basis of XRD data) in the complex of selenourea with triphenylphosphinegold(I) chloride **76** ($\text{MX}_n = \text{Ph}_3\text{PAuCl}$).¹⁹⁴

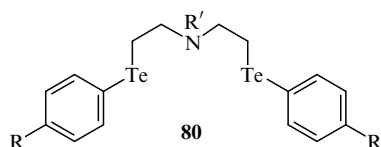
The interest in complexes containing N,Te-donor ligands has increased recently, although individual examples of such compounds had been examined also in earlier investigations.^{18, 81, 193, 195–197} A series of studies^{198–211} (among them a review²⁰⁴) devoted to complexes of ligands with N,Te-donor centres have been published during the last six years. However, the problem of competitive coordination was not discussed in these publications. In our view, this can be explained by the fact that in most other investigations conditions were created for the monodentate M–Te coordination of the ligands considered or for the formation of N–M–Te metalocycles. Thus, owing to the high donor activity of the chalcogen atom and the steric effects preventing the occurrence of M–N coordination, the ligand behaves as a monodentate Te-donor in the tellourea complex **77**,¹⁹⁵ as in the thio- and seleno-analogues examined above.



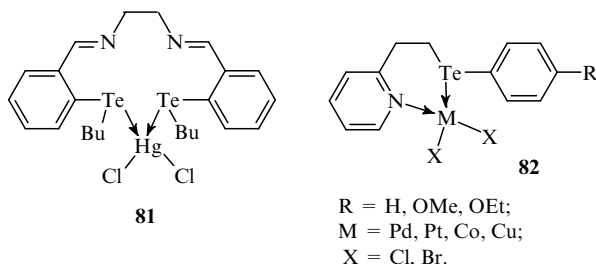
The steric effect apparently prevents the involvement in chelation of the potentially bidentate ligand **78**, the mercury bromide complex of which has the structure **79** according to X-ray diffraction data.²⁰¹



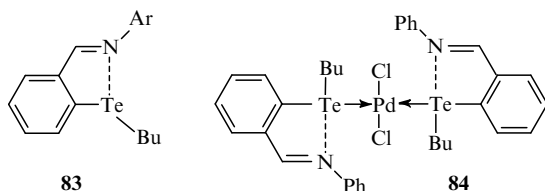
At the same time, it is believed²⁰³ that ligands **78** and **80** form with rhodium(I) and rhodium(III) chlorides chelate structures having N,Te-coordination.



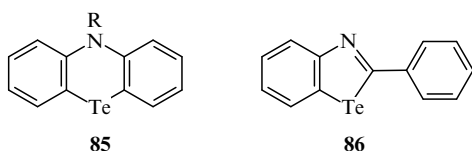
The formation of the chelate structure **81** has been demonstrated by X-ray diffraction.²¹² A similar structure is characteristic also of type **82** complexes.^{207, 209}



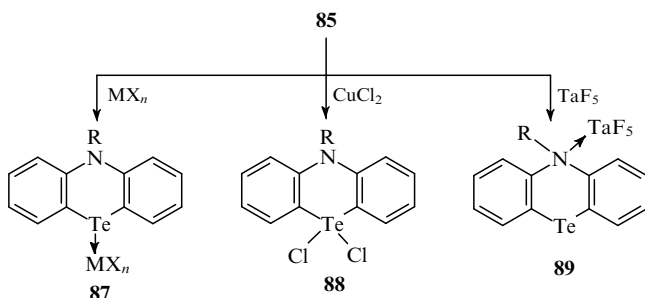
The tellurium-containing azomethines **83** must also be regarded as potential N,Te-chelating ligands.²¹³ However, the ligand system in the palladium dichloride complexes obtained from them behaves as a Te-monodentate system, forming, in particular, complex L_2PdCl_2 with structure **84**.²¹⁰



Although the location of the coordinate bond in complex **84** is justified from the standpoint of the HSAB principle, one cannot rule out that the decrease in the denticity of ligand **83** can be accounted for by the formation of the intramolecular Te...N bond,^{212, 217} which virtually deprives the azomethine nitrogen atom of the possibility of becoming coordinated to the metal. Ligands **85**^{18, 218} and **86**²¹¹ are free from the above disadvantages.

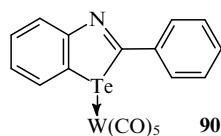


A cycle of reactions of *N*-alkyltellurazines **85** has been achieved with Pearson acids: soft (MX_n = rhodium carbonyl chlorides, palladium, silver, and mercury halides) (with formation of complexes **87**), intermediate ($CuCl_2$) (with formation of complex **88**), and hard (TaF_5) (with formation of complexes **89**).^{18, 219}

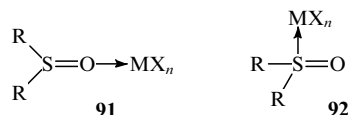


The structures of the products formed have been justified by IR and NMR spectroscopic data and by studying their chemical behaviour.^{18, 196} In conformity with the HSAB principle,¹⁸ ligand **86** (L) interacts with chromium, molybdenum, and tungsten (M) hexacarbonyls to form complexes of the type $LM(CO)_5$ with a

M–Te bond, which has been rigorously demonstrated²¹¹ by X-ray diffraction in relation to complex **90**.

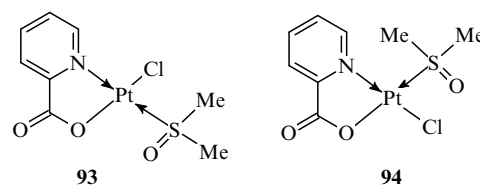


Fairly numerous publications have been devoted to complexes with ambident ligands containing O, S-donor centres.^{2, 18, 103} Those devoted to the competitive reaction of organosulfoxides, especially dialkyl(aryl) sulfoxides forming O-bonded (compounds **91**)^{220–227} and S-bonded (compounds **92**)^{228–239} isomers are outstanding among them.



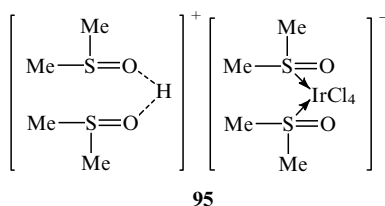
The occurrence of O→M coordination **91** has been demonstrated by X-ray diffraction in relation to complexes of dimethyl sulfoxide (DMSO) with trichlorodiphenylantimony(V)²²⁰ and zirconium tetrachloride,²²² ionic complexes of osmium,²²³ and heterometallic compounds.^{224–227}

It also follows from X-ray diffraction data that S→M bonding is characteristic²²⁸ of the isomeric adducts of DMSO and the platinum chelate complexes of pyridine- α -carboxylic acid **93** and **94**.

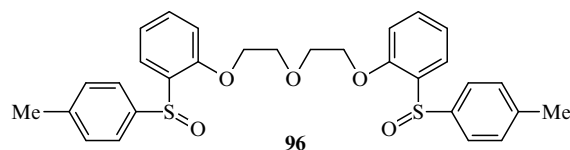


The same type of coordination is observed in the complexes $\{[Pt(NH_3)_4][PtCl_3(DMSO)]_2\}$,²²⁹ $\{[PtCl_3(DMSO)_2L]DMSO\}$,²³⁰ $[Pt(DMSO)(CH_3CN)Cl_2]$,²³¹ $[Pt(DMSO)(Py)Cl_2]$,²³² $\{K[Pt.(Et_2SO)Br_3]\}$,²³³ $[RuCl_2(DMSO)_3(NH_3)]$, $\{[Ru(DMSO)_2.(NH_3)_2]H_2O\}$,²³⁴ $\{[H(DMSO)_2]^+[RuCl_4(DMSO)_2]^- \}$,²³⁵ $\{[H(DMSO)_2]^+[OsNO(DMSO)Cl_4]^- \}$.²³⁶

We may note that the structure containing the $[H(DMSO)_2]^+$ cation had been described earlier for the complex between iridium chloride and DMSO.²³⁷



S,S'-Coordination has also been observed in the complex between palladium chloride and the podand **96**.²³⁸



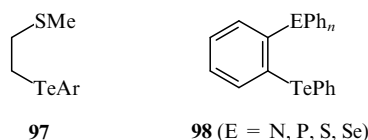
It has been suggested that several types of coordination of the ligand (O-, S-, or bridging O,S-coordination) may occur simultaneously in the DMSO complexes. It is believed²³⁹ that such a situation is observed in complexes of dibenzyl and tetramethylene sulfoxides of the type $[PtL_2Cl_2]$ and $[ML_3Cl_3]$, where M = Ru(III), Rh(III), and Ir(III). Finally, we may draw attention to the

extremely unexpected result obtained in a study²⁴⁰ of the structure of the complex $\{[\text{EuL}_3\text{Phen}(\text{H}_2\text{O})_2]\text{DMSO}\}$, where $\text{L} = \text{C}_5\text{H}_4\text{NCO}_2^-$ is the anion of nicotinic acid. In this complex, the DMSO molecule is not involved in coordination with the metal but forms a hydrogen bond with the oxygen atom of one of the coordinated water molecules.

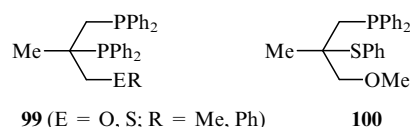
Analysis of the data presented shows that in virtually all cases DMSO is coordinated in accordance with the HSAB principle: hard Pearson acids are bound to the oxygen atom and soft acids are bound to the sulfur atom.

There are comparatively few examples of complexes containing O,Se- or O,Te-donor atoms.^{18, 204} It is believed that the M–O bond is mainly formed in dimethyl selenoxide complexes.¹⁸ It is so far difficult to discuss competitive coordination in the series of O,Te-containing compounds presented,^{204, 216, 241–243} since there are no structural data for the few available O,Te-containing ligands which have not been used to obtain complexes.^{18, 204, 241, 244, 245}

In conclusion of this section we may note that the review of Singh and Srivastava²⁰⁴ contains data on the complexes of a series of ligands containing the N-, P-, S- and Se-donor atoms in addition to tellurium, for example, compounds **97** and **98**.

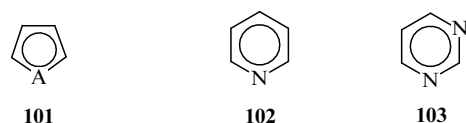


Ligands **99** and **100**, containing three donor atoms, are not without interest in connection with the problem of competitive coordination under discussion.²⁴⁶



4. Heteroaromatic compounds and their derivatives

Heteroaromatic compounds belong to ambident $\sigma, \sigma', \sigma, \pi$ -, and π, π' -ligand systems,^{247–249} which interact with metals or their salts and also with organometallic derivatives to form complexes in which these ligands are bound to the metal atom either *via* the heteroatom or *via* the π -system.^{2, 18–21} When competitive coordination is considered, the ligands of this type can be usefully divided into two varieties:^{19–21} π -excess and π -deficient ligands. According to the literature,^{250, 251} five-membered heterocyclic compounds of type **101**, in which the number of π electrons exceeds the number of atoms in the ring, belong to ligands of the first variety. These are pyrrole (**101**: A = NR; R = H, Alk, Ar), phosphole (**101**: A = PR), arsole (**101**: A = AsR), stibole (**101**: A = SbR), furan (**101**: A = O), thiophene (**101**: A = S), selenophene (**101**: A = Se), and tellurophene (**101**: A = Te) ligand systems. The ligands of the second type include pyridine (**102**) and other six-membered nitrogen-containing heterocycles (azines) with one or several heteroatoms (**103**). The azoles **104** can be formally^{250, 251} assigned to π -excess systems.

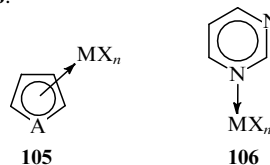


A = NR, PR, AsR, SbR, O, S, Se, Te.



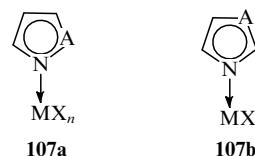
A = NR', O, S, Se, Te; R = H, Alk, Ar, benzo.

It has been shown in numerous investigations that the π -excess ligand systems form mainly type **105** $\eta^5(\pi)$ -complexes, while π -deficient ligands give rise to $\eta^1(\text{N})$ -metallo-derivatives of type **106**.



A = NR, PR, AsR, SbR, O, S, Se, Te.

The azole ligands behave in complex formation reactions as π -deficient species (complexes **107a, b**).



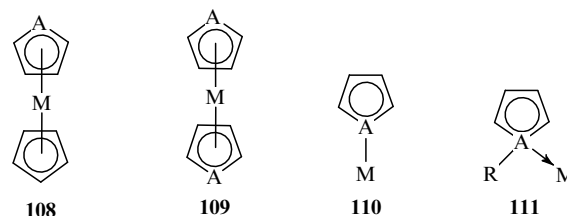
A = NR, O, S, Se.

It will be shown below that, although these rules hold for numerous examples of complexes of heteroaromatic ligand systems, there are quite a few complexes of type **101** and **102** ligands with a non-traditional location of the coordinate bond.

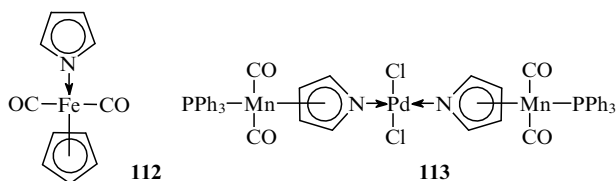
a. Complexes of five-membered heterocycles containing one heteroatom

Reviews^{19, 20, 84, 252} and other publications^{18, 253} contain numerous examples indicating the formation of type **105** $\eta^5(\pi)$ -complexes based on pyrrole (A = NR), phosphole (A = PR), arsole (A = AsR), stibole (A = SbR), thiophene (A = S), selenophene (A = Se), and tellurophene (A = Te). Fragments of metal carbonyls, mainly $\text{Mn}(\text{CO})_3$ and $\text{Cr}(\text{CO})_3$, usually serve as the Lewis acids MX_n .

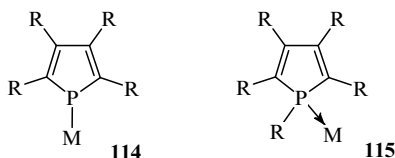
In addition to complexes of this type, sandwich structures of type **108** and **109** are quite widely represented among η^5 -coordinated systems.



The $\eta^1(\sigma)$ -coordinated structures **110** and **111** have been obtained mainly from pyrroles **105**: A = NR, R = H, Alk, Ar) and phospholes (**105**: A = PR, R = H, Alk, Ar). Apart from the N-metal-substituted compounds **110** (see, for example, Refs 253 and 254), the organometallic compounds **112** and **113** have been described²⁰ among the N-coordinated pyrrole complexes.

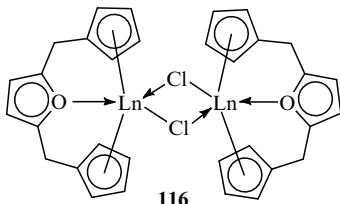


The P-coordinated phosphorus complexes are represented,^{20, 84, 255, 256} by structures of two types (**114** and **115**), structure **114** being more common than structure **115**.



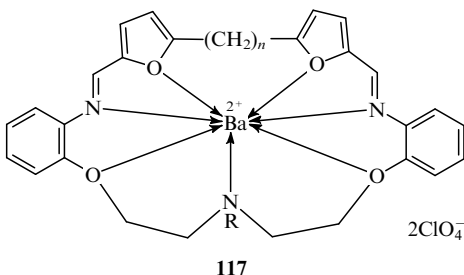
We are not aware of type **110** and **111** complexes in the arsole (A = As), stibole (A = Sb), and bismuthole (A = Bi) series.

The question of the possibility of the involvement in coordination of the furan ring oxygen atom remains unelucidated. We may note in this connection a recently published communication²⁵⁷ in which the hitherto unique example of a complex with a O—M coordinate bond is described (complex **116**).



In the absence of X-ray diffraction data, the structure of compound **116**, described on the basis of IR and ¹H NMR spectroscopic studies,²⁴⁷ gives rise to doubt.

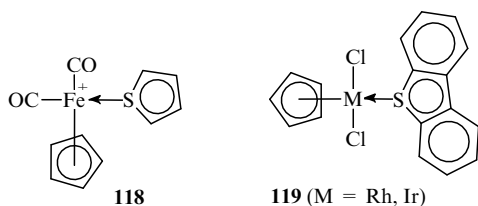
The involvement in coordination of the furan ring oxygen atom forming part of the composition of macrocyclic ligands, for example compound **117**, is more realistic.²⁵⁸



R = Alk, CH₂CH₂OAlk.

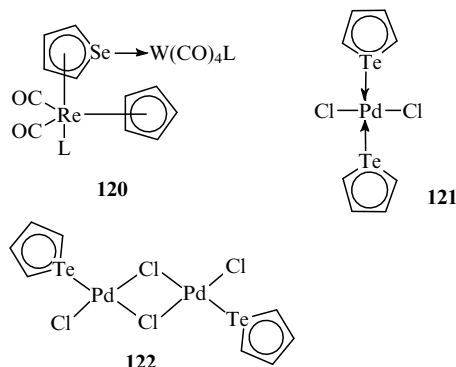
The stabilisation of structures **116** and **117** is apparently associated with chelate and macrocyclic effects.²⁵⁹ We may also note that an organometallic compound with a M—C bond may be formed from furan (see, for example, Selna and Merob²⁶⁰).

In contrast to furan complexes, thiophene complexes with the sulfur-centred coordinate bond are represented by a large set of structures.^{20, 261} In particular, such coordination has been observed in the ionic complex **118**.²⁰



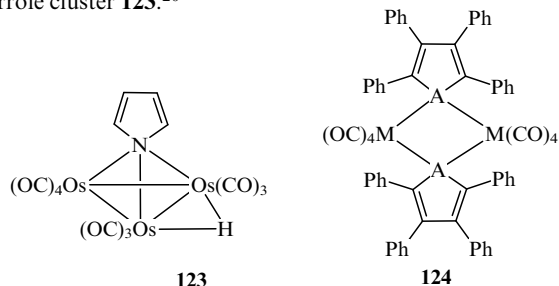
$\eta^1(\text{S})$ -Coordination is also characteristic of the dibenzothiophene complexes **119**.²⁶²

An example of the involvement in coordination of the selenophene Se atom (complex **120**) is known.²⁶³



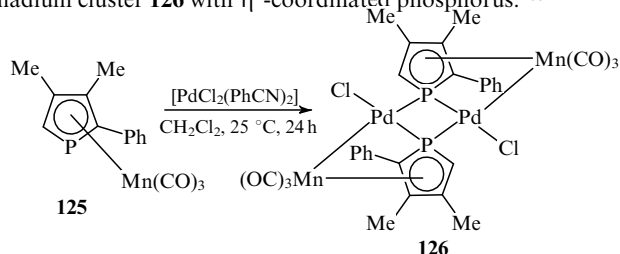
$\eta^1(\text{Te})$ -Coordinated tellurophene complexes are represented by the palladium chloride compounds **121** and **122**, the structures of which have been frequently considered, for example in reviews.^{81, 193, 195} A similar coordination has apparently been observed in complexes of tellurium-containing heterocycles with univalent and trivalent rhodium chlorides and carbonyl chlorides.²⁶⁴

In a number of instances, type **101** ligand systems behave as bidentate and even tridentate ligands.²⁰ Complexes have been formed in which A(σ)- or A(σ), π -metal bonds are formed. Such nonstandard $\eta^3(\text{N}, \sigma)$ -coordination has been observed in the pyrrole cluster **123**.²⁰

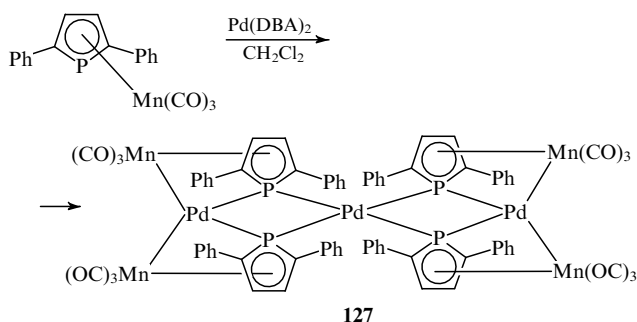


M = MN, Re; A = P, As.

Complexes with η^2 -coordinated phosphorus are particularly widely represented in the series of phosphole and its derivatives.²⁰ In particular, such coordination has been observed in the manganese and rhenium dimers **124**.²⁰ The reaction of 3,4-dimethyl-2-phenylphosphocymantrene **125** with the benzonitrile complex of palladium dichloride in methylene chloride afforded the dinuclear palladium cluster **126** with η^2 -coordinated phosphorus.²⁶⁵

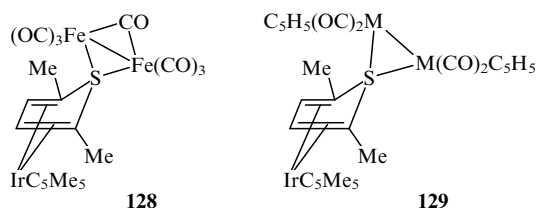


The same type of coordination of phosphorus occurs in the trinuclear cluster **127** obtained in the course of the following reaction:²⁶⁵

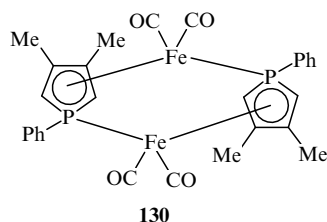


DBA = dibenzylideneacetate anion.

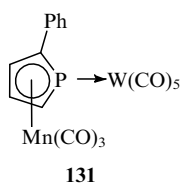
η^2 -Bonding is observed also in the analogous arsole complexes **124** (A = As)²⁰ and also in the thiophene complexes **128**²⁶⁶ and **129**.²⁶⁷



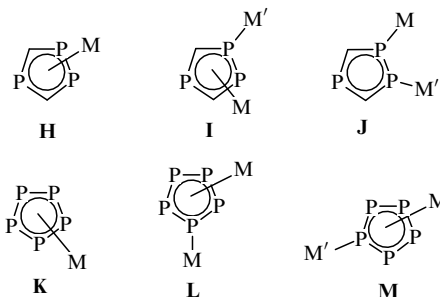
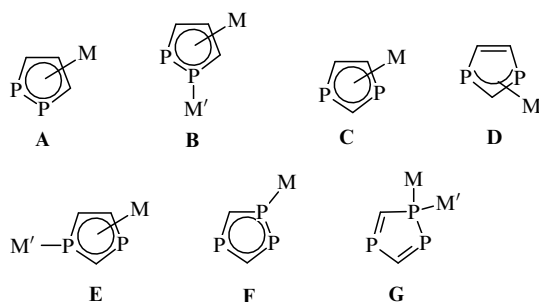
In this connection, we may mention the polymeric iron complex of pyrrole in which the heterocycle is involved in coordination of the $\eta^1(\sigma)$ - and $\eta^5(\pi)$ -types.^{20, 268} The same coordination is characteristic²⁰ of phosphole complexes, for example compound **130**.



A heteronuclear complex of *C*-phenylphosphocymantrene with tungsten pentacarbonyl (compound **131**), in which phosphole also behaves as a σ, π -donor ligand system, has been described.²⁶⁹



The complexes of phospholes containing several phosphorus atoms in the heterocycle are quite widely represented.⁸⁴ The possible variants of their bonding to metals are presented below (structures **A** – **M**).⁸⁴



Other examples of complexes with heterocycles **101** bound to the metal in different ways have been described in reviews^{20, 270} and other communications.^{271–274}

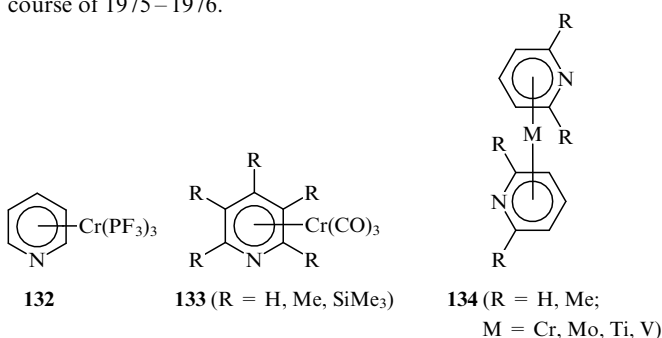
b. Complexes of azines

The commonest and well known mode of coordination of pyridine and other six-membered nitrogen-containing heterocycles is N(σ)-bonding to the metal, which is indicated by the early reviews.^{18, 19, 275–277} Among the studies published in recent years, we shall mention data concerning the complexes of N-coordinated pyridine with BH_2CN ²⁷⁸ and the ruthenium-cyclopentadienyl fragment²⁷⁹ and a series of publications by Italian investigators^{280–284} devoted to the properties and structures of the adducts of pyridine and chelates modelling the fragments of biologically important systems (in particular vitamin B₁₂) and the corrole complex of iron.²⁸⁵

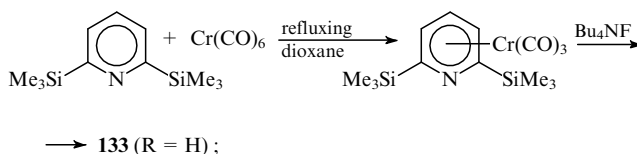
The structure of the adduct of pyridine and copper(II) acetate, in which N – Cu coordination also occurs, has been revised.²⁸⁶

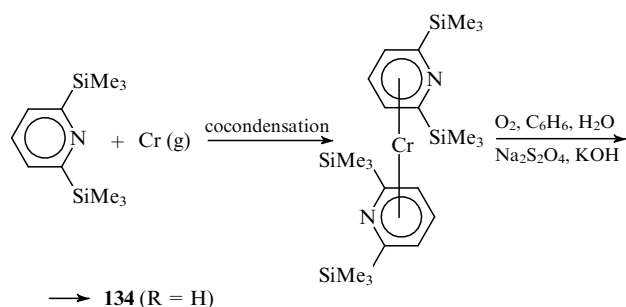
Studies in which the metal is coordinated to several pyridine molecules with formation of the complexes MPy_n are of interest.^{287, 288} The $\eta^1(\text{N})$ -coordination of pyridine in the dinuclear rhodium complexes $[\text{Rh}_2(\text{MeCOO})_3\text{Py}_4]\text{CF}_3\text{SO}_3$ and $[\text{Rh}_2(\text{MeCOO})_2\text{Py}_6](\text{CF}_3\text{SO}_3)_2$ has been demonstrated by X-ray diffraction.²⁸⁹

The $\eta^1(\text{N})$ -coordination of azines was believed to be the only one possible up to the middle of the 1970s, to a considerable extent as a result of the unsuccessful attempt to obtain $\eta^6(\pi)$ -coordinated pyridine complexes by Fischer — a Nobel Laureate.²⁹⁰ However, the unusual $\eta^6(\pi)$ -complexes of pyridine **132**,²⁹¹ **133**,^{292, 293} and **134**^{294–296} were synthesised in independent investigations in the course of 1975–1976.



Complexes of types **133**²⁹⁷ and **134**²⁹⁸ with unsubstituted pyridine (R = H) were later obtained and in both cases trimethylsilylpyridine derivatives served as the starting compounds.

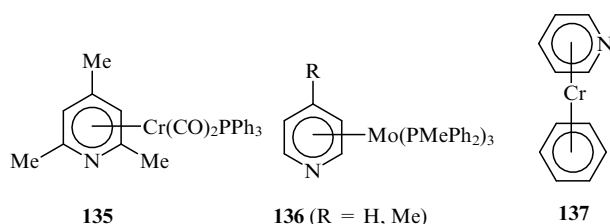




We may note that the direct gas-phase synthesis of the type **132** and **134** π -complexes of pyridine from the zerovalent metals played a decisive role.^{299, 300}

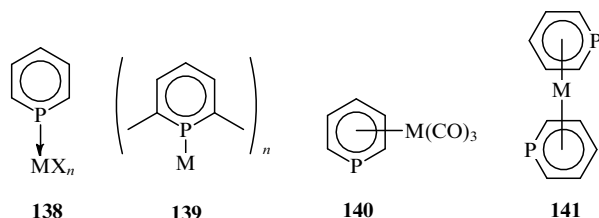
The η^6 -2,4,6-collidine(triphenylphosphine)chromium dicarbonyl complex **135** has been synthesised³⁰¹ and characterised by X-ray diffraction.³⁰²

Complexes similar to complex **132** have also been obtained from molybdenum (complex **136**³⁰³).

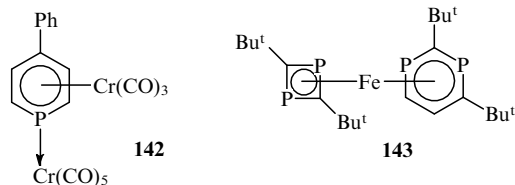


The mixed-ligand complex **137** has been obtained by the gas-phase cocondensation of three components — pyridine, benzene, and zerovalent chromium.²⁹⁸

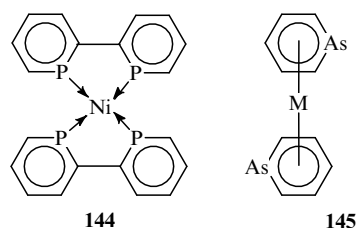
The complexes of the phosphorus analogue of pyridine — phosphabenzene — (compounds **138**–**141**) are represented by a fairly wide range of compounds. Among them, the coordination compounds **138**^{304, 305} and **139**^{306–309} are $\eta^1(\sigma)$ -coordinated, while compounds **140**^{304, 310} and **141**^{304, 311, 312} are $\eta^6(\pi)$ -coordinated.



Complex **142**, in which mixed $\eta^1(\sigma)$ - and $\eta^6(\pi)$ -coordination of 4-phenylphosphabenzene occurs,³⁰⁴ and the heteroligand sandwich complex of four- and six-membered diphosphorus heterocycles **143**²⁷⁴ are also of undoubted interest.



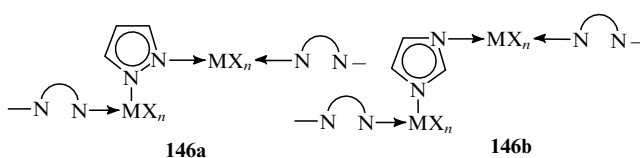
α, α' -Diphosphaphenyl (the phosphorus analogue of α, α' -bipyridyl) is bound to nickel in a way similar to that in compound **139**³¹³ with formation of complex **144**.



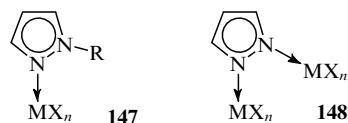
Complexes of $\eta^6(\pi)$ -coordinated arsa-1,3,5-cyclohexatriene **145** (M = Cr,³¹⁴ Ti,³¹⁴ and V³¹⁵) have been described.

c. Coordination compounds of azoles

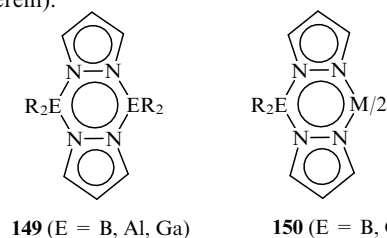
Until recently, it was believed that, in contrast to the heterocycles **101** and the azines **102** and **103**, azoles form only complexes in which the ligands are bound to the metal *via* the N atom of the pyridine ring. The ligand systems then behave as monodentate species (**107**)^{1–3, 18, 21, 189, 276, 316–318} or perform a bridging function (**146**).^{21, 139, 276, 319–323}



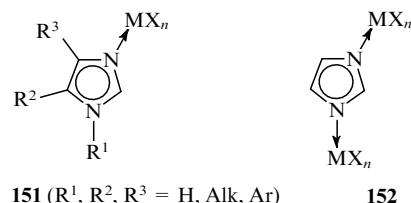
$\eta^1(\sigma, N)$ -Bonding to the metal has been observed in the pyrazole complexes **147**^{21, 189, 317, 318, 324, 325} and **148**.^{41, 319–323, 326–330}



Type **149** organoelement derivatives of pyrazoles^{1, 21, 139} and numerous complexes¹⁵⁰ obtained from them are of special interest (see the relevant reviews^{21, 321–323} and the literature quoted therein).

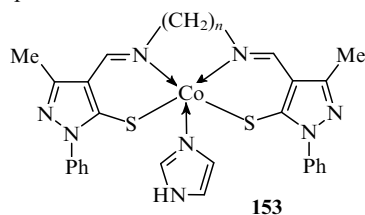


Like the pyrazole complexes, the imidazole complexes are represented by structures **151** (monodentate coordination of the ligand)^{1–3, 318, 331–339} and **152** (bridging coordination).^{1, 2, 340–342}

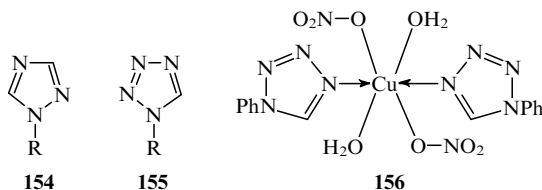


Among the studies devoted to imidazole (L) complexes, we shall mention the following: the unexpected formation of the monomeric copper acetate complex CuAc₂L₂,³³⁴ the synthesis of

previously unknown complexes ZnS_6L_2 and ZnSe_4L_2 ,³³³ and also the isolation of the imidazole adduct of the chelate pyrazole complex **153**.³³⁹

**153**

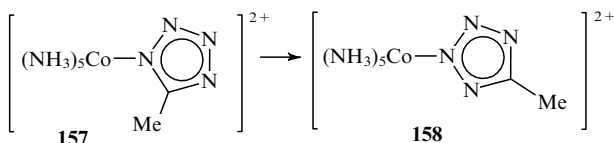
$\sigma(\text{N})$ -Coordination is characteristic also of 1,2,4-triazoles **154**³⁴³ and tetrazoles **155**.^{344, 345}

**154****155****156**

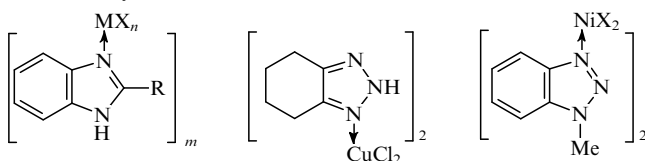
We emphasise that the tetrazole fragment in the dinitrodiaquobis(phenyltetrazole)copper(II) complex is coordinated *via* the N(4) atom of the heterocycle (complex **156**).³⁴⁴

1-Ethyltetrazole **155** ($\text{R} = \text{Et}$) is bound to the metal *via* the same donor centre in the complex with copper dinitrate.³⁴⁵

The bond isomerisation (**157** $\rightarrow$ **158**) observed in the cations of 5-methyltetrazole complexes of pentamminecobalt(III) is of undoubted interest in connection with the problem of competitive coordination.^{346–348}

**157****158**

As in the case of azoles, the metal complexes of the benzo-analogues of azoles are N-coordinated compounds. For example, such coordination is characteristic of 2-substituted derivatives of benzimidazole **159**,^{1, 189, 317, 349} tetrahydrobenzotriazole **160**,³⁵⁰ and 1-methylbenzotriazole **161**,³⁵¹ *i.e.*



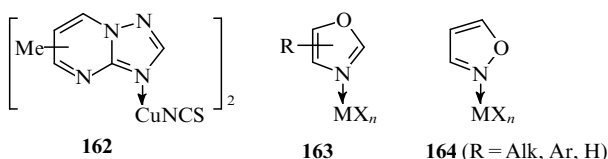
159 ($\text{R} = \text{H, Et, Pr, Pr}^i, \text{Bu}$;
 $\text{M} = \text{Co, Ni}$;
 $\text{X} = \text{NCS, ClO}_4$;
 $m = 2, 3$)

160

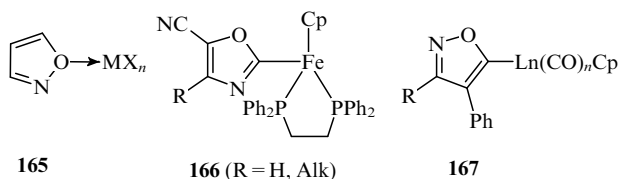
161
 $(\text{X} = \text{Cl, Br, NCS, NO}_3)$

The $\eta^1(\text{N})$ -coordination in complexes **160**³⁵⁰ and **161**³⁵¹ ($\text{X} = \text{NO}_3$) has been demonstrated by X-ray diffraction.

A type of binding of the metal analogous to that in complex **160** occurs in the copper complex of 5(6)-methyl-1,2,4-triazolo[1,5a]pyrimidine **162**.¹⁴⁴

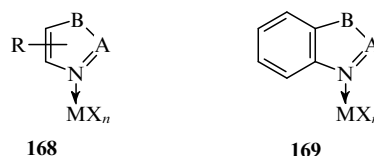
**162****163****164** ($\text{R} = \text{Alk, Ar, H}$)

The N–M coordination also occurs in oxazole and isoxazole complexes^{352, 353} (complexes **163** and **164**). At the same time, the possibility of the involvement of the O atom of the oxazole ring (complex **165**) has been discussed.³⁵³ In our view, this donor atom can hardly compete with powerful nucleophilic centres such as the N atom.

**165****166** ($\text{R} = \text{H, Alk}$)**167**

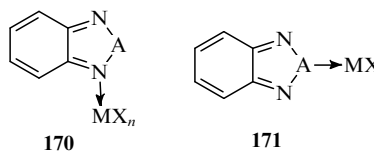
C-Organometallic derivatives of oxazole **166**³⁵⁴ and isoxazole **167**³⁵⁵ are of undoubted interest.

The complexes of chalcogen-containing azoles, for example complex **168**, N–M and benzazoles, for example complex **169**, contain mainly N–M bonds.^{1, 2, 189, 336, 356–364}

**168****169**

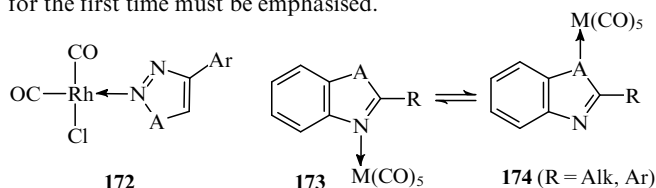
$\text{A} = \text{CH, N}$; $\text{B} = \text{O, S, Se}$.

The location of the coordinate bond in the complexes of benzo-2,1,3-thiadiazole and of its selenium analogue (coordination types **170** and **171**) has aroused an especially great deal of controversy.

**170****171**

$\text{A} = \text{S, Se}$.

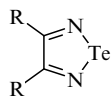
At the same time, X-ray diffraction studies indicate unambiguously^{359, 360} that only type **170** N–M coordination occurs in the coordination compounds under consideration. The same mode of coordination is characteristic of the rhodium chloride dicarbonyl complexes of 1,2,3-thiadiazole and 1,2,3-selenodiazole (coordination type **172**).³⁶¹ In connection with the data under discussion, the X-ray diffraction studies^{211, 365} in which direct evidence for the possibility of the involvement of the tellurium atom of benzotellurazole in coordination to the metal (complex **90**) was obtained for the first time must be emphasised.

**172****173****174** ($\text{R} = \text{Alk, Ar}$)

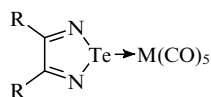
$\text{A} = \text{S, Se, Te}$.

This type of coordination can probably be accounted for by the high electron-donating activity of the tellurium atom in the complexes of N,Te-containing ligands, which were considered previously in the present review.

In connection with the problem of the competitive reaction of chalcogenazoles with metals, it appears important to carry out X-ray diffraction studies on a series of metal carbonyl complexes of benzothiazole **173** ($\text{A} = \text{S}$) and benzoselenazole **173** ($\text{A} = \text{Se}$), for which the equilibrium **173** $\rightleftharpoons$ **174** exists in solution according to ¹H NMR data.³⁶⁶ Furthermore, it appears important to carry out specific studies on the complex formation reactions of other tellurium-containing azole ligands for the same purpose.^{196, 367, 368} In particular, the deliberately synthesised tellurodiazole **175**, from which complexes **176** with a Te–M bond, hitherto unknown in the series of chalcogenodiazoles (*cf.* complexes **170** and **171**), may be obtained with a high degree of probability, is of undoubted interest.



175

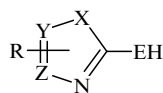


176 (M = Cr, Mo, W)

d. Complexes of exocyclic substituted heteroaromatic ligands

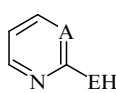
The complex formation reactions of heteroaromatic ligands with coordination-active groups result in the formation, apart from the metal derivatives of types **106** and **107** examined above, also of complexes involving exocyclic groups and also bimetallic complexes involving two donor centres.

Particularly numerous data indicating the occurrence of these types of coordination of heteroaromatic ligand systems with coordination-active side substituents have been obtained in relation to complexes of amino- and hydroxy(chalcogen hydride)-derivatives of five- and six- membered heterocycles of types **177** and **178**.



177

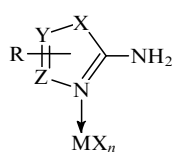
X = NR', O, S, Se;
Y, Z = CR, N;
R = H, Alk, Ar, benzo;
E = NH, O, S, Se, Te.



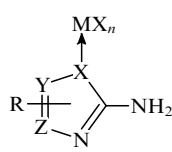
178

A = CH, N;
E = NH, O, S, Se, Te.

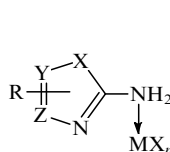
Aminoazoles **177** and aminoazines **178** (E = NH) are involved in both monodentate (**179–183**) and bidentate bridging (**184** and **185**) binding of the metal.



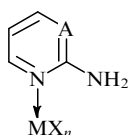
179



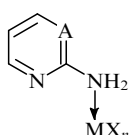
180



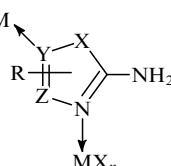
181



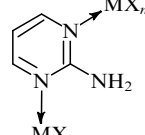
182



183



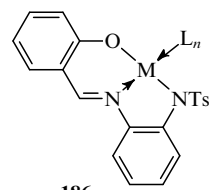
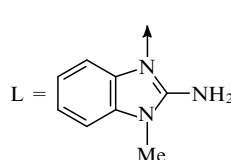
184



185

The coordination types **179** and **182** are the most common.³⁵ Apart from the extensive compilation of data presented by Garnovskii *et al.*³⁵, there are data on the type **179** structure obtained by X-ray diffraction for the 2-aminoimidazole complexes of copper dichloride³⁶⁹ and dibromide³⁷⁰ and of the 2-aminothiazole complex of zinc dichloride.³⁷¹ The same type of location of the coordinate bond arises from the quantum-chemical interpretation of the regioselective coordination in the series of metal complexes of 2-aminoazoles.^{372–374} In contrast to earlier calculations,³⁷⁴ Garnovskii and coworkers^{372,373} determined the relative thermodynamic stabilities of the bond isomers **179–181**³⁷² and their geometry.³⁷³ The preferential N-coordination (type **179**) of the proton and BH₃ arises also from the results of quantum-chemical calculations³⁷⁵ by the MNDO method.

The location of the coordinate bond at the N atom (type **179**) is also characteristic³⁷⁶ of more involved complexes, for example of the adducts of 2-amino-1-methylbenzimidazole (L) with the chelate complexes of tridentate Schiff bases (complex **186**).

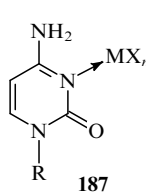


186

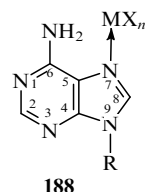
M = Cu, Co; n = 1, 2.

These complex adducts are of interest because they have been obtained electrochemically.^{376,377} Complexes of aminoazoles with a bridging function of type **184** have been described.^{35, 141, 378–380}

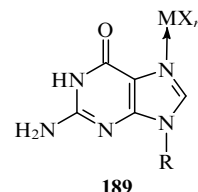
The complexes of aminopyridines **182** (A = CH),^{35, 130, 382, 385–390} and fragments of biologically important systems (amino-derivatives of pyridine)–cytosine **187**,^{35, 38, 381, 391–396} adenine **188**,^{35, 38, 381, 397, 398} and guanine **189**^{399,400} — are represented by a wide range of structures in which metal salts are coordinated *via* endocyclic N atoms of the pyridine type.



187

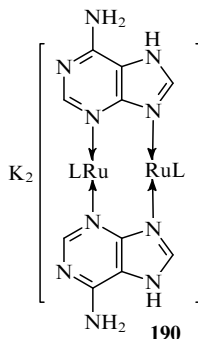


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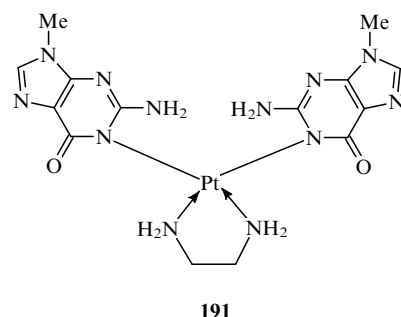


189

Apart from complex **188**, the formation of the dimeric ruthenium complex **190** involving the N(3) and N(9) atoms has been postulated⁴⁰¹ for adenine **188** (R = H) on the basis of ¹H NMR data. According to X-ray diffraction data, the bridging type of binding of this ligand with deprotonation of the NH group of the imidazole ring and the formation of a tetranuclear η⁶-benzeruthenium(II) cluster is also possible.⁴⁰²



190

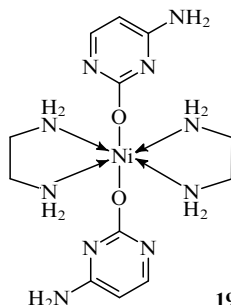


191

L = EDTA anion.

Coordination of type **189** is mainly characteristic of guanine.^{35, 38, 381, 399} At the same time, complexes in which guanine is coordinated *via* the N(1) atoms and also *via* the N(1) and N(7) atoms are known.⁴⁰³ Thus the complex of 9-methylguanine with ethylenediamineplatinum(II) has the structure **191**.⁴⁰³

We may note⁴⁰⁴ the very unexpected O-coordination of cytosine in complex **192**. In this case, the ligand is coordinated in the enolic tautomeric form.

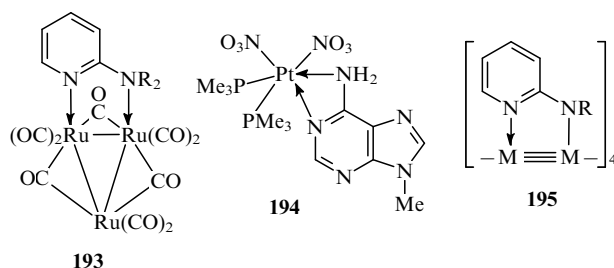


192

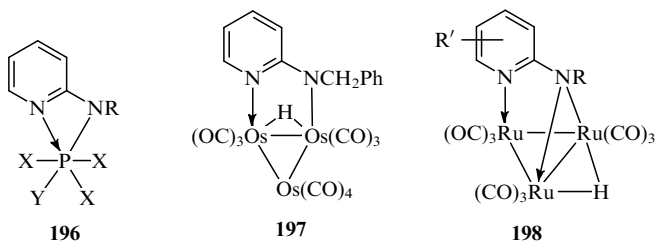
In the series of complexes of aminoazoles and aminoazines, there is virtually no direct evidence for the formation of structures **181** and **183** with a coordinated NH_2 group, although in individual instances such types of coordination have not been ruled out from consideration.^{35, 353}

Numerous studies have been devoted to heterocyclic amino-complexes in which the ligand is bound *via* two donor centres: nitrogen atoms of the pyridine type and an unaltered or deprotonated amino-group. The interest in this type of complex arose a fairly long time ago,^{35, 405} mainly in connection with the formation in the latter of multiple metal–metal bonds,^{405, 406} but the greatest number of complexes with this type of coordinate bonds have been obtained recently.^{35, 406–418}

η^2, μ -Coordination with the simultaneous binding of an endocyclic nitrogen atom and the nitrogen atom of an amino-group occurs in the following complexes: for example, in the ruthenium cluster **193**,³⁵ in the trinuclear complex adduct $\{[\text{Ru(III)Ru(III)Ru(II)OAc}_6\text{L}_3]\text{L}'_3\}$, where $\text{L} = 2\text{-aminopiperazine}$ and $\text{L}' = \text{EDTA}$,⁴¹⁶ in the platinum(II) nitrate complex of 9-methyladenine and trimethylphosphine **194**,^{418, 419} and in the silver complex $[\text{Ag}_3(\text{Py}-\text{NH}_2)_4(\text{NO}_3)_4]$.⁴¹⁹



The structure of metal clusters of type **195** with a deprotonated amino-group has been discussed in a number of publications.^{35, 405, 406} Both mononuclear^{35, 414, 418} and polynuclear^{35, 407, 415} complexes have been noted among complexes with a deprotonated NHR group. In particular, complexes of 2-methylamino- and 2-(2'-pyridyl)aminopyridines **196** with pentavalent phosphorus halides and CF_3 -substituted derivatives may be assigned to the former.⁴¹⁴



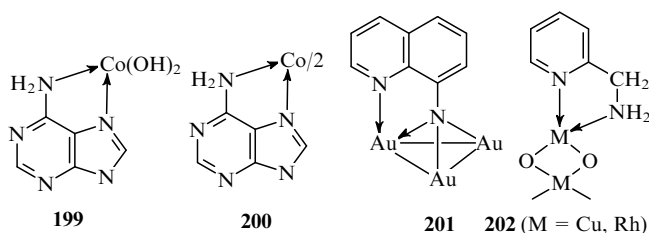
$\text{R} = \text{Me}, 2\text{-Py}; \text{X} = \text{F}, \text{Cl};$
 $\text{Y} = \text{F}, \text{Cl}, \text{CF}_3.$

$\text{R} = \text{H}, \text{Me}, \text{Ph}; \text{R}' = \text{H}, \text{Me}.$

Cluster structures of the type considered, for example **197**, have been discussed in a review.³⁵ The nitrogen atom of the NR fragment may participate in the simultaneous bonding to two metal atoms, forming trinuclear clusters which are very common among aminopyridine complexes of ruthenium (complexes **198**).^{408–413}

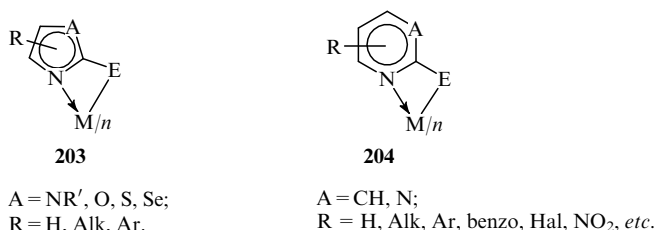
Instances of substitution of a hydrogen atom of the NH_2 group by a metal atom are also known in the series of other aminoheterocycles, for example in cytosine³⁵ and in 9-amino-acridine.⁴²⁰

In conclusion, we may note that the involvement of both nucleophilic N centres in coordination is characteristic of aminoheterocycles where the disposition of the pyridine and amine nitrogen atoms promotes the formation of chelate structures. Such a structure was first proposed for cobalt complexes of adenine **199** and **200**.³⁵

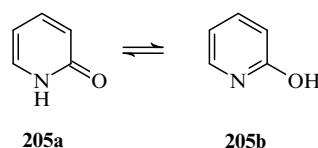


The formation of structures with a N, N' -five-membered metalocycle was later demonstrated in relation to trinuclear and tetranuclear gold(I) clusters with 8-aminoquinoline **201**⁴²¹ and polymeric copper and rhodium acetate clusters **202**.⁴²²

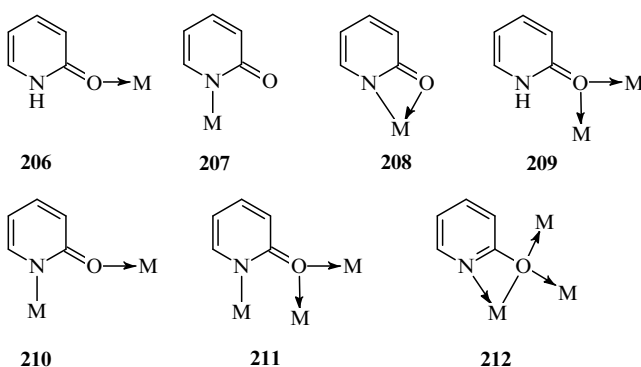
A wide variety of structures is characteristic of complexes obtained from type **177** and **178** ligand systems containing O, S, and Se donor centres in the exocyclic substituent. Metalocyclic (chelate) structures of types **203** and **204** ($\text{E} = \text{O}, \text{S}, \text{Se}$) are most common among them.^{423–425}



The coordination chemistry of oxygen-containing ligands, represented mainly by the pyridinone **205** complexes, has been examined in another review⁴²⁵ and will not be discussed in detail here.

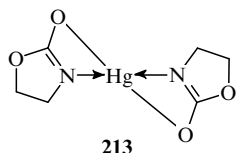


Rawson and Winpenny⁴²⁵ examined the mononuclear (**206–208**), dinuclear (**209** and **210**), and trinuclear (**211** and **212**) binding of metals by the ligand **205**, taking into account tautomerism of the type $\text{205a} \rightleftharpoons \text{205b}$.

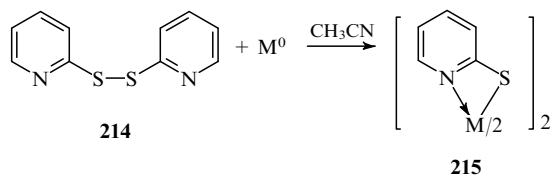


They paid particular attention⁴²⁵ to the bridging function performed by the ligands **205** in complexes with multiple metal–metal bonds.

It is noteworthy that chelate structures of type **208** are fairly common among complexes **203** and **204** with an endocyclic oxygen substituent ($\text{E} = \text{O}$). A metalocyclic structure **213** of this type occurs, for example, in the mercury complex of 1,3-oxazolidin-2-one.⁴²⁶

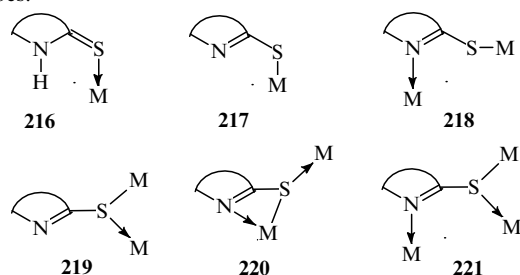


Chelate structures of types **203** (E = S)^{423, 424–430} and **204**^{423–425, 431–441} are quite widely represented among complexes of 2-mercapto-derivatives. These compounds are obtained preferentially in the interaction of type **177** and **178** ligands with metal salts^{423–425, 427–430} and also from disulfides (for example, compound **214**) and zerovalent metals under the conditions of electro-synthesis.^{432–437, 440}

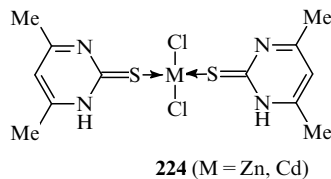
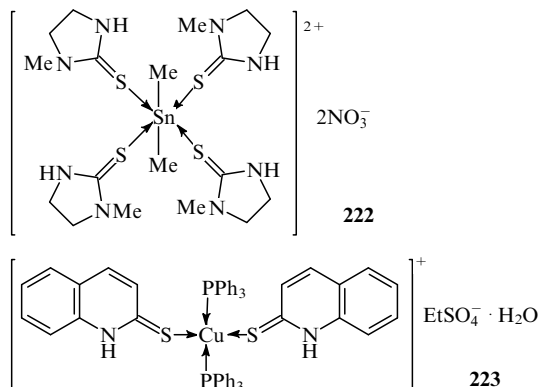


Apart from complexes **215**, adducts of the type $ML_2 \cdot nL'$ are formed in the presence of various N-bases (L'), where LH = mercaptoazoles or mercaptoazines and $L' = \text{Py}$, Bipy, *o*-Phen and other N-donors.^{299, 431, 432, 437, 438} It has been shown recently⁴⁴¹ that a transformation of the type **214** → **215** can be achieved not only under the conditions of electrosynthesis but also in chemical syntheses carried out for zerovalent lanthanides (samarium and yttrium) in tetrahydrofuran (THF) in the presence of hexamethylphosphamide.

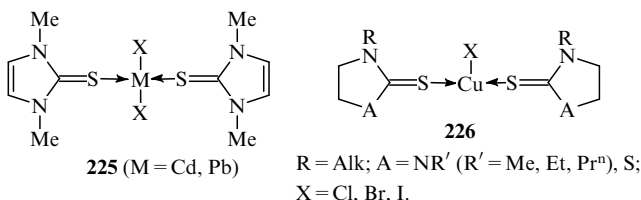
The presence of N- and E-donor centres in the ligands considered and also prototropic tautomerism lead to the occurrence of various structures of the complexes of mercaptoazoles and mercaptoazines, which can be represented by the following types:



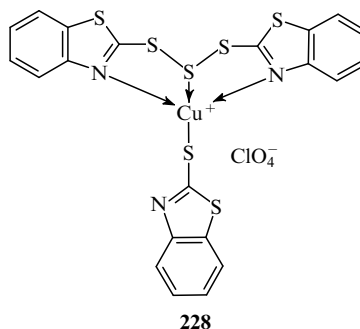
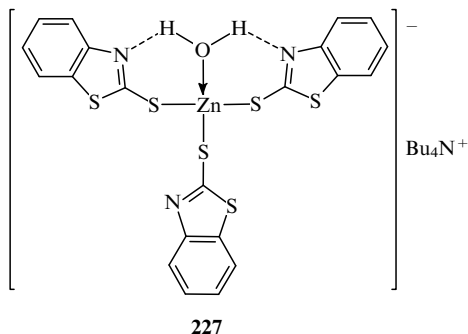
Compounds **216**, which behave as monodentate thione ligands (LH), are represented by a fairly large series of complexes having the composition $(LH)_mMA_n$ (see the relevant review⁴²³ and the subsequent publications, for example, Refs 442–444). Complexes obtained from 1-methyl-2(3*H*)-imidazolinethione **222**,⁴⁴² quinoline-2-thione **223**,⁴⁴³ and 4,6-dimethylpyrimidine-2-thione **224**⁴⁴⁴ have been characterised structurally among them.



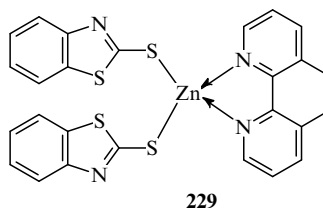
Naturally the $=S \rightarrow M$ coordination is observed in metal complexes with fixed thione forms of the ligand — in the complexes of 1,3-dimethyl-2(3*H*)-imidazolinethione **225**,⁴⁴⁵ *N*-alkylimidazolidine-2-thione **226** (A = NR'),⁴⁴⁶ and thiazolidine-2-thione **226** (A = S).⁴⁴⁶



The number of structurally characterised complexes of type **217** with the thiol form of the ligand, which is of interest because chelate structures are not formed with its participation, is significantly smaller. Such monodentate S-coordination has been observed in the anion of the complex $\{[Bu_4N]^+[ZnL_3]^- \cdot H_2O\}$ **227**⁴²³ and in the cationic complex of an unusual trisulfide derivative of benzothiazole **228**.

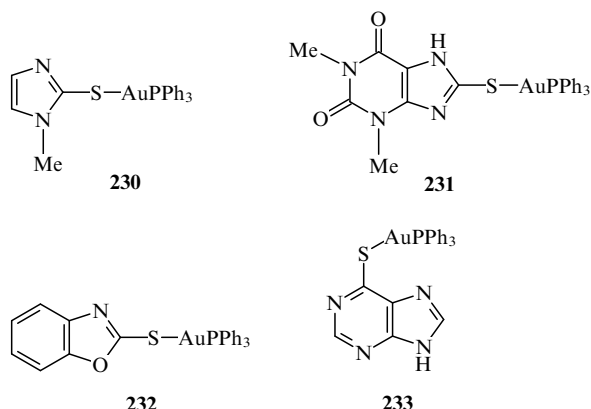


X-Ray diffraction data have shown⁴⁴⁰ that such mononuclear binding of the ligand is characteristic also of the adduct of the zinc salt of 2-mercapto-benzothiazole with *o*-phenanthroline (compound **229**).

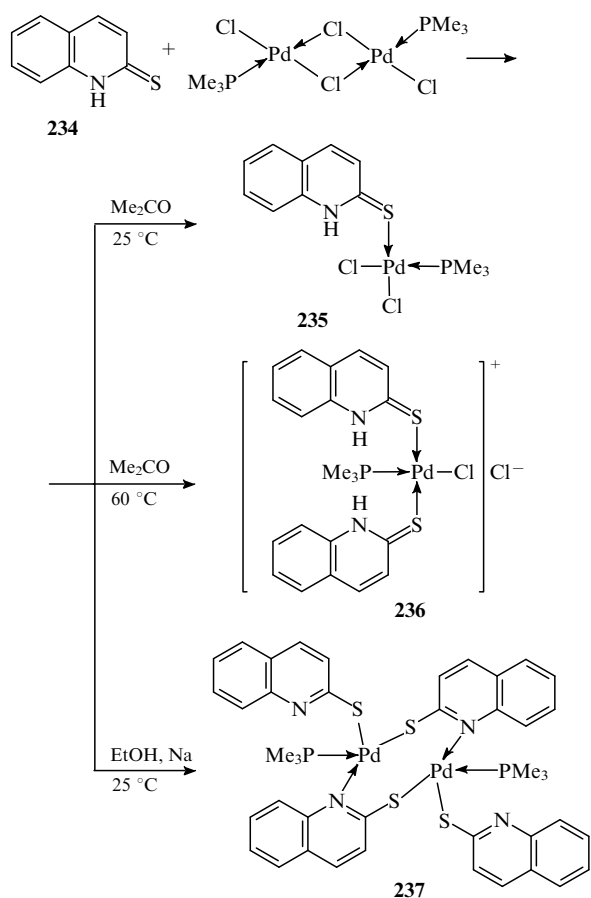


In connection with the $\eta^1(S)$ -monodentate coordination of 2-mercaptoazoles being discussed, we may note that the same type of binding of the metal is observed in complexes of triphenylphos-

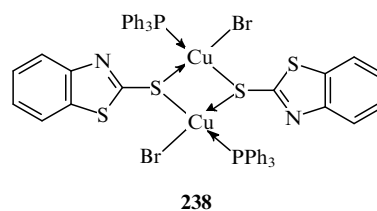
phinegold with 2-mercapto-1-methylimidazole **230**,⁴⁴⁷ 8-mercaptotheophylline **231**,⁴⁴⁸ 2-mercaptobenzoxazole **232**,⁴⁴⁹ and purine-6-thiol **233**.⁴⁵⁰



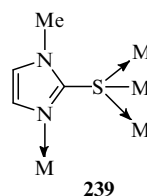
Structures **218** with bridging N,S-coordination are quite common for the dinuclear complexes of the heterocycles considered.^{423, 451–454} Studies^{451, 454} in which the detailed influence of the complex formation reaction conditions on the type of complexes formed was detected are of special interest. In particular, a scheme has been published⁴⁵¹ showing that molecular mono-S-coordinated adducts **235** and **236** with the thione tautomeric form of the ligand and the dinuclear complex **237** in which the thiol and bridging binding of the ligand system occur simultaneously may be obtained for the same ligands, for example compound **234**, depending on the nature of the solvent, temperature, and the pH of the medium.



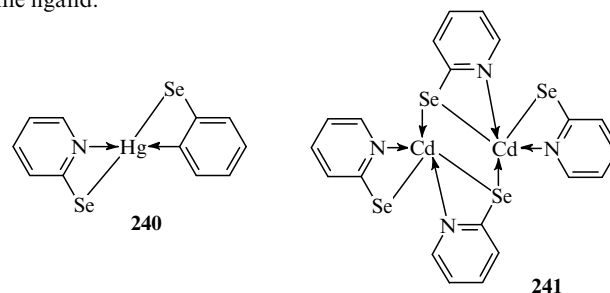
Coordination of type **219** has been observed in a series of complexes,^{423, 455, 456} for example in the recently described dimeric copper complex of benzothiazole **238**.⁴⁵⁶



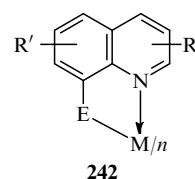
In this connection, we may point out that, in the dodecanuclear cluster $[\text{Cu}_{10}\text{Cu}_2(\text{C}_4\text{H}_5\text{N}_2\text{S})_{12}(\text{MeCM})_4]$, where $\text{C}_4\text{H}_5\text{N}_2\text{S}$ = 2-mercapto-1-methylimidazole, the thiol sulfur can participate simultaneously in coordination with three copper atoms.⁴⁵⁷ The coordination of type **239**, not considered previously, in which the above imidazole derivative behaves as a tetradentate bridging ligand, occurs in this instance.



The same type of bonding has been established⁴⁵⁸ for the clusters $\text{Ru}_9\text{H}_3(\text{Py})(\text{CO})_{21}$. The complexes of the selenium-containing analogues **203** and **204** ($\text{E} = \text{Se}$) are represented by single investigations. For example, it has been demonstrated by X-ray diffraction⁴⁵⁹ that the mercury complex of pyridine-2-selenol has the structure **240**, whereas the chelate and bridging configurations occur simultaneously in the cadmium dimer **241** obtained from the same ligand.



When the disposition of the donor centres is favourable for the formation of the metallocycle, the hydroxy-, mercapto-, and hydroseleno-derivatives form chelate structures like the amino-substituted nitrogen heterocycles examined above. They are represented particularly widely among complexes of 8-hydroxy- and 8-mercapto-quinolines **242** ($\text{E} = \text{O}$ ^{424, 460, 461} and $\text{E} = \text{S}$ ^{424, 462–467}). Thus the chelate complexes **242** ($\text{E} = \text{O}$; $\text{R} = \text{H}$, Alk ; $n = 3$) of trivalent indium, gallium, thallium, cobalt, antimony,⁴⁶⁰ osmium, ruthenium, and rhodium⁴⁶¹ have been synthesised from 8-hydroxy-quinoline and its substituted derivatives (LH) and characterised structurally. The complexes have an octahedral structure and contain the $\text{C}_2\text{H}_5\text{OH}$ (In, Ga, Co), H_2O (Te), and CHCl_3 (Os, Ru, Rh) molecules as additional ligands. The antimony complex does not contain other molecules and has the composition SbL_3 .

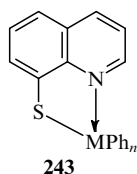


$\text{E} = \text{O}, \text{S}$.

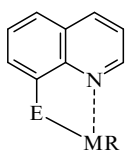
Data on the structures of nickel, cobalt, copper, zinc, and cadmium bishydroxyquinolates (type **242**, $n = 2$) are presented in a review⁴²⁴. The structures of nickel,⁴⁶² indium,⁴⁶³ palladium,⁴⁶⁵ rhodium,^{464, 466} and iridium⁴⁶⁷ 8-mercaptoquinolates

were described subsequently. We may note the synthesis and the rigorous demonstration of the structures of two heterovalent complexes between vanadyl and 8-mercaptoquinoline (LH):⁴⁶⁸ in one of them, having the composition $(VL_3)^-(PPh_4)^+$, the vanadium entering into the composition of the anion has a oxidation state of two, whilst in the other, neutral complex having the composition VL_3 , the oxidation state of vanadium is three. The above oxidation states of vanadium have been confirmed by magnetochemical measurements: the experimental magnetic moment is 3.73 B.M. for the first of the above complexes and 2.78 B.M. for the second.

Organometallic derivatives of 8-hydroxyquinoline^{469–473} and 8-mercaptoquinoline^{470,474–477} are of special interest. Judging from the literature data,^{424,470–477} the question of the denticity and the modes of coordination of 8-mercaptoquinoline in mercury,^{469,471,473} gold,^{472,474–476} tin,⁴⁷⁰ lead,⁴⁷⁰ and antimony⁴⁷⁷ complexes is controversial. It has been suggested^{470,477} that the chelate structure **243**, which is standard for 8-mercaptoquinoline, occurs in these complexes.



243

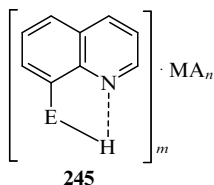


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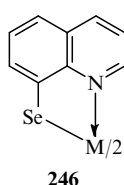
M = Sn, Pb, Sb; $n = 2, 3$. M = Hg, Au; R = Ph, PPh_3 ; E = O, S.

At the same time, a non-standard coordination interaction has been proposed for complexes of 8-hydroxy- and 8-mercaptoquinolines with phenylmercury and triphenylphosphinegold fragments (complex **244**): the presence of only one covalent E—M bond and the formation of a secondary N...M bond.^{471–473,474–476}

Apparently the coordination in the molecules of the adducts of 8-hydroxy- and 8-mercaptoquinolines with Lewis acids (complex **245**) should also be non-standard. However, although their synthesis has in fact been achieved,²² we are not aware of data on the structures of these complexes.



245



246

By analogy with molecular complexes of *o*-hydroxyazomethines,^{22,23} the remaining option is to assume that the coordinate bond in the adducts **245** can be located on the donor atom E. The structures of complexes of 8-hydroselenoquinoline are not clear either, although the chelates **246** themselves have been known for a fairly long time.¹⁸²

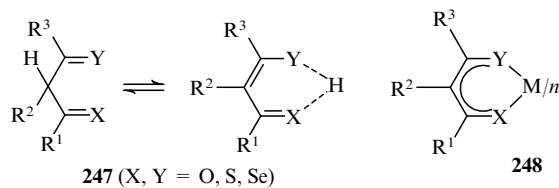
So far as we are aware,^{76,193,195,368} the complexes of telluroderivatives of types **203** and **204** (E = Te) have not been described.

5. Competitive coordination of chelating ligands

Competitive coordination in the series of chelating ligands leads to the formation of structures of several types and to intrachelate isomerism involving the closure of metalocycles with different numbers of 'members'. This aspect of competitive coordination has been most clearly investigated in relation to complexes of β -diketones, *o*-hydroxyazomethines, and their structural analogues.

a. Complexes of chelating ligands

It is well known that β -diketones and their thio- and selenoanalogues **247** give rise to metal chelates of type **248** on interaction with metal salts^{4,103,478,482} and under the conditions of gas-phase synthesis or electrosynthesis.^{299,483}

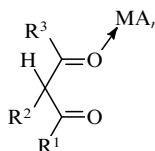


247 (X, Y = O, S, Se)

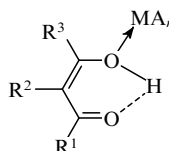
248

The structure of type **248** β -diketonates (X = Y = O) has been demonstrated by X-ray diffraction.^{478,481,484–501} The structures of copper,^{485–487,499–501} tungsten,^{493,494} yttrium,^{489,496} and lanthanides^{490,491,496–498} β -diketonates have been investigated. Type **248** (X = O, Y = S) metal chelates are formed¹⁰³ also in the case of monothio- β -diketones. It has been suggested that chelate complexes of dithio- β -diketones **248** (X = Y = S) have a structure similar to that of the β -diketonates.¹⁰³

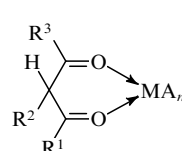
Together with the above mode of coordination, other (chelate and nonchelate) types of binding of the ligands have been observed for complexes of β -diketones. Coordination can be achieved with participation of the oxygen atom as well as the carbon atom or with participation of both donor centres. Similar types of coordination (**249–262**) have been frequently discussed in a number of publications.^{4,24,31,481,484,502,503}



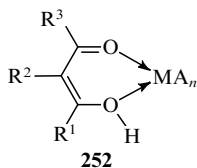
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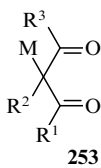
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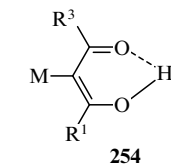
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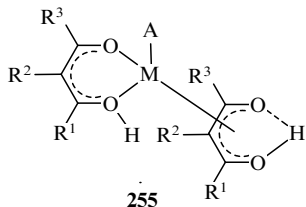
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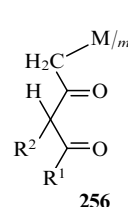
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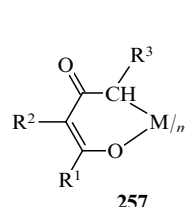
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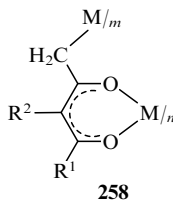
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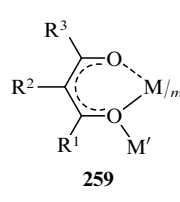
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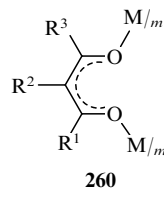
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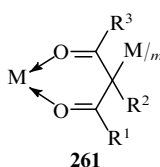
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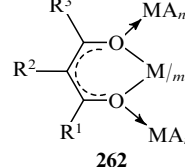
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260



261

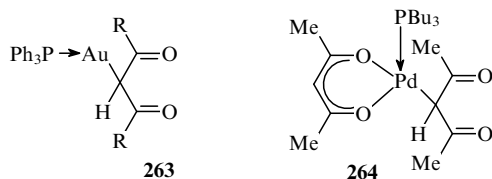


262

It follows from the data presented in a review⁴⁸⁴ that an unusual monodentate type **250** O-coordination occurs in the complexes $Mn(HAA)Br_2$ and $Re(HBA)Cl(CO)_3$, where HAA = acetylacetone and HBA = benzoylacetone, while the diketone form of acetylacetone **251**, coordinated as a bidentate species, is encountered in the chelates $\{[Ni(HAA)_2]Br_2\}$ and $\{[Ni(HAA)_2(H_2O)_2](ClO_4)_2\}$.⁴⁸⁴

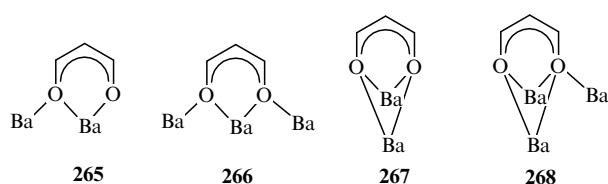
Among the mononuclear β -diketone C-coordinated complexes, we shall differentiate univalent gold compounds **263**,

having a structure of type **253**, which have been recently obtained and characterised structurally.^{504–507}



It has been suggested⁵⁰⁸ that a structure with acetylacetonate fragments of type **255** coordinated in different ways is characteristic of complex **264**, but rigorous evidence for its occurrence is lacking.

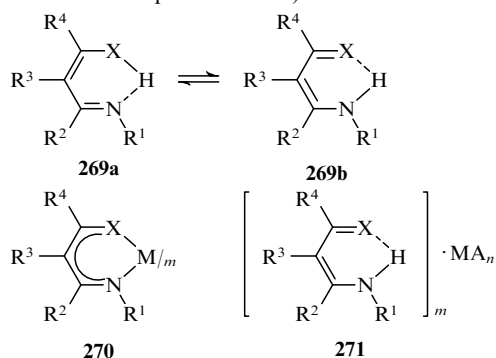
The complexes of β -diketones with additional O-coordinations have been discussed in relation to dinuclear and trinuclear barium complexes.^{509,510} Their coordination units can be represented by formulae **265–268**.



We emphasise that the β -diketone fragment behaves as a tridentate ligand in complex **265** and as a tetradentate ligand in complexes **266** and **267**. However, in contrast to complex **266**, a bischelatate structure occurs in complex **267**.^{511–514} Structure **267** has been detected by X-ray diffraction in the barium complexes of the dipivaloylmethane anion (DPM): $\text{Ba}_2(\text{DPM})_4(\text{NH}_3)_4$,⁵¹¹ $\text{Ba}(\text{DPM})\text{Et}_2\text{O}$,⁵¹² $\text{Ba}_4(\text{DPM})_8$,^{509,513} and $\text{Ba}_2(\text{DPM})_4(\text{Bipy})_2$.⁵¹⁴ The structure with the fragment **268** has been noted in the complex $\text{Ba}_5(\text{DPM})_9\text{H} - \text{DPM}$. According to Drozdov and Trojanov⁵¹³, it contains a pentadentate dipivaloylmethane anion.

According to the information available to us, structures similar to **249–268** are unknown in the series of chalcogen-containing analogues of β -diketones. Such complexes have apparently not been obtained.

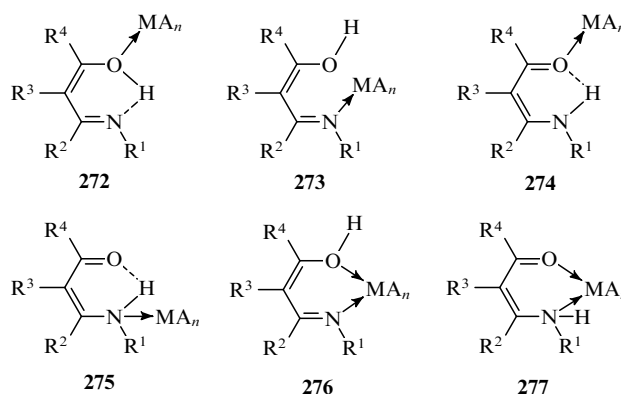
A situation similar to that described above for the β -diketone complexes observed also for *o*-hydroxyazomethines and their structural analogue **269** (see the relevant reviews^{22,23,33,34,503} and the literature quoted therein).



$\text{X} = \text{NR}^5$ ($\text{R}^5 = \text{H, Alk, Ar, Het, Ts}$), O, S, Se.

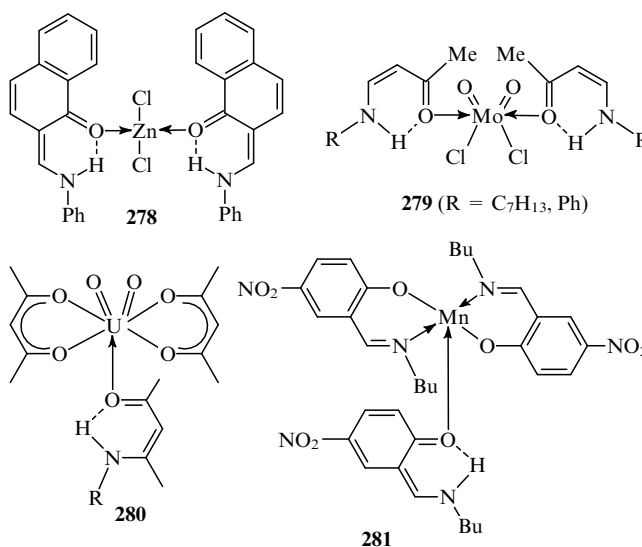
The accumulated literature data show that type **269a,b** ligands form mainly type **270** chelate compounds ML_m ($m = 1-4$). The chelates obtained from ligands **269a,b** ($\text{X} = \text{O}$) and 3d metals — cobalt,^{23,515} nickel,^{23,516–519} copper,^{23,520,521} and zinc^{23,522} — are the most common.

The complexes in which the ligands **269** are involved in type **271** bonding are less well known. In this case, neutral azomethine molecules function as the ligands.^{22,23,34} Taking into account the tautomerism of ligands **269a,b** ($\text{X} = \text{O}$)^{23,33} and intramolecular hydrogen bonding,²³ structures with non-standard formation of a coordinate bond were attributed to these complexes.



In complexes **272–275**, *o*-hydroxyazomethines **269** ($\text{X} = \text{O}$) and their structural analogues ($\text{X} = \text{NR}^4$, S) behave as monodentate ligands, whereas they are involved in bidentate coordination in complexes **276** and **277**.

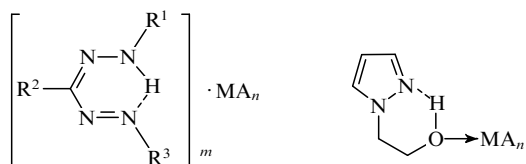
Conclusions concerning the modes of coordination of the ligands in type **271** adducts indicated above have been reached mainly on the basis of data obtained in comparative studies of the IR spectra of these complexes and the corresponding ligands **269**, which is not sufficiently rigorous.²² X-Ray diffraction studies have demonstrated unambiguously that, out of the six structures **272–277**, only one (**274**), containing the monodentate azomethine ligand in the ketoamine tautomeric form and having an intramolecular hydrogen bond, is actually formed. This situation has been established, for example, for the zinc chloride complex of 2-oxo-1-naphthylideneaniline (complex **278**)⁵²³ and the molybdenum dioxide chloride complexes of β -aminovinyl ketones (complexes **279**)^{524,525} and also in the case of adducts of uranyl acetylacetonates with acetylacetonate imine **280**⁴⁸⁴ and the type **281** manganese complexes of salicylaldimines.⁵²⁶



The coordination of salicylaldimines *via* the oxygen atom in type **281** complexes has been confirmed by the O-binding of these ligands to various metal salts.⁵²⁷

The molecular complexes **271** of structural analogues of β -aminovinyl ketones — β -aminovinylimines **269** ($\text{X} = \text{NR}^4$) and β -aminovinyl thiones **269** ($\text{X} = \text{S}$) — have been described.^{22,23} However, the structures of these molecular complexes have not been investigated by X-ray diffraction, so that the location of the coordinate bond in them remains obscure.

Molecular complexes are also formed by other chelating ligands, for example by formazans **282** and *S*-hydroxy- and *S*-mercapto-quinolines **245** ($\text{X} = \text{Y} = \text{S}$).²²

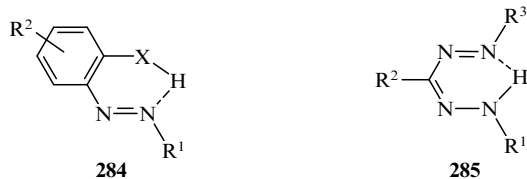
282 ($R^1, R^2, R^3 = \text{H, Alk, Ar, Het}$)

283

Interesting results have been obtained in a study⁵²⁸ in which a molecular complex of 1-ethylenedihydroxypyrazole **283** was described and characterised structurally.

b. Intrachelate isomerism

In the presence of several donor atoms in the chelating unit of the ligand, the possibility of their competitive reaction and of the closure of metalocycles with different numbers of members arises. This type of competitive coordination is particularly characteristic of the azo-compounds **284** and the formazans **285**.

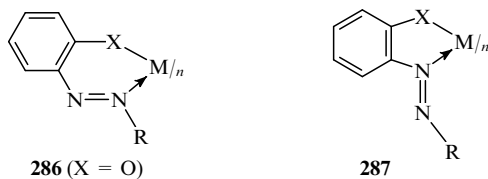


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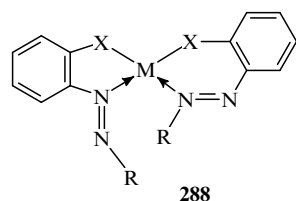
285

$X = \text{NR}^3$ ($R^3 = \text{H, Alk, Ar, Ts}$), O, S;
 $R^1 = \text{Ar, Het}$;
 $R^2 = \text{H, Alk, Ar, benzo, Hal, NMe}_2$, etc.

It is well known that six-membered metalocycles **286** ($X = \text{O}$) are produced in chelate complexes of *o*-hydroxyazobenzenes.^{34, 529}

286 ($X = \text{O}$)

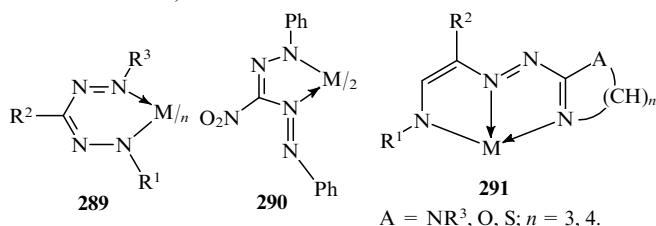
287



288

At the same time, when $X = \text{NR}$ or S, five-membered chelates are formed together with six-membered ones.^{23, 34, 530, 531} The number of members in type **287** chelate compounds is determined by the nature of not only the donor atom X but also of the metal. Thus, according to X-ray diffraction data, when $X = \text{S}$ five-membered metalocycles are formed in the nickel and zinc complexes, whereas five- and six-membered chelate units are produced in the palladium complexes **288** (see the relevant review³⁴ and the literature therein).

A similar situation is characteristic of complexes formed by type **285** formazan ligands, which afford chelate complexes of type **289–291** depending on the nature of the substituents R and the metal (see the relevant reviews,^{37, 532} a communication,⁵³¹ and the literature therein).



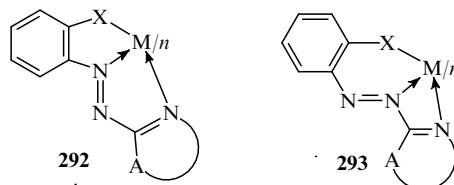
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290

291

$A = \text{NR}^3, \text{O, S}; n = 3, 4.$

Another type of intrachelate isomerism is associated with the formation of metalocycles, differing in the number of members in complexes of heteroarylmino(hydroxy)azo-compounds.⁵³¹ In the case of ligands of this type, one has to expect, apart from type **286–288** coordination ($R = \text{Het}$), the involvement of the N atoms of the hetero-fragments in additional bonding to the metal with formation of complexes **292** or **293** (see Garnovskii *et al.*⁵³¹ and the literature quoted therein).

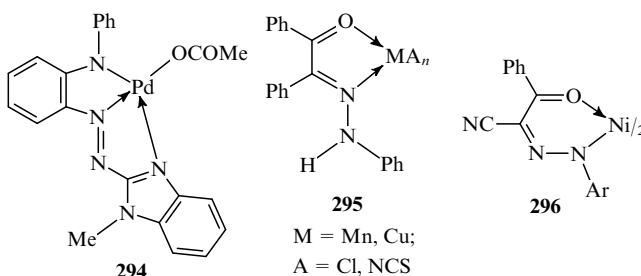


292

293

$X = \text{NR, O}; A = \text{CH, N}.$

The controversy, extending over a period of many years, concerning the formation of five-membered (complexes **292**) or six-membered and four-membered (complexes **293**) metalocycles has been recently resolved in favour of the first combination by solving the structure of the palladium complex **294**.⁵³¹



294

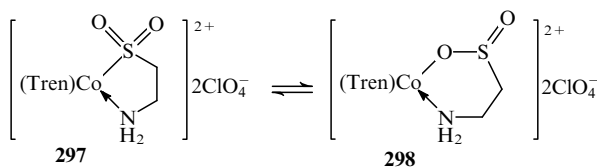
295

296

$M = \text{Mn, Cu};$
 $A = \text{Cl, NCS}$

Bond isomerism involving different ring sizes has been observed also in the case of the monohydrazones of β -dicarbonyl compounds. Thus complex **295**, with a five-membered metalocycle, has been described in a monograph,⁵³³ while the structure of the six-membered hydrazone metal chelate **296** was established in another study.⁵³⁴

An interesting instance of chelate isomerism **297**→**298** has been observed in cobalt complexes of aminoethanesulfonates.⁵³⁵ Not only the ring size in the coordination unit but also the ligand environment changes in these complexes.

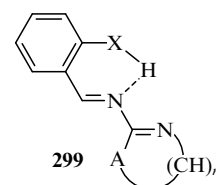


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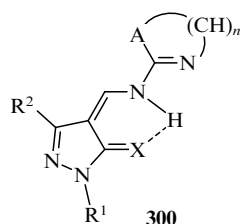
Tren = tri(2-aminoethyl)amine.

The competitive coordination of bidentate and polydentate chelating ligands occupies an important place in modern coordination chemistry.⁵³⁶ With the aid of these ligands, it is possible to vary the number and nature of the donor centres involved in bonding with the metal. The potentially tridentate ligands of type **299–301** are convenient models for the study of competitive coordination of this type.

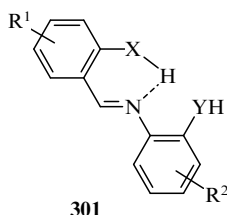


299

$X = \text{NTs, O};$
 $A = \text{N, O, S}, n = 3, 4.$

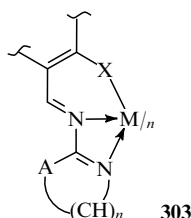
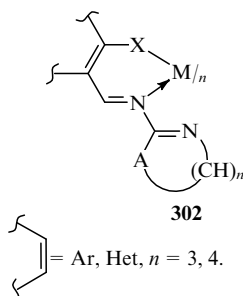


X = NTs, O, S, Se;
R¹, R² = H, Alk, Ar, Het;
A = N, O, S; n = 3, 4.

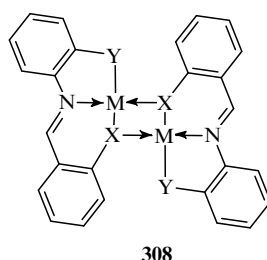
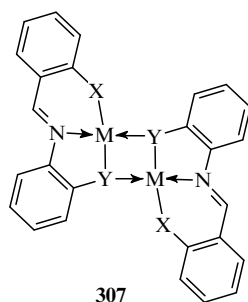
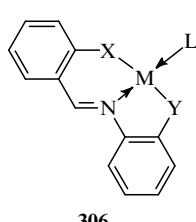
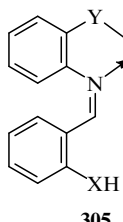
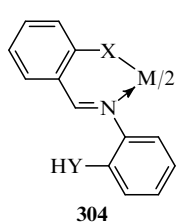


X, Y = NTs, O, S;
R¹, R² = H, Alk, Ar.

Analysis of published data (see the relevant reviews^{23,34}) shows that the denticity of type **299** and **300** ligands depends on the structure of the chelates which they form: bidentate coordination without the involvement of the nitrogen atom of the heterocycle in the binding of the metal is characteristic of planar complexes (complex **302**), whereas additional coordination to the nitrogen atom of the heterocycle is observed in tetrahedral structures (complex **303**).



Structures **304**–**308** may be attributed to the complexes of ligands **301** on the basis of the structure of the latter (X = Y = O)⁵³⁷ and data^{23,34} indicating the formation of six-membered and five-membered metallocycles by azomethine ligands.



So far as we are aware, the mononuclear complexes **304** and **305** have not so far been described. The formation of structures **306**^{538–544}, **307**,^{545,546} and **308**⁵⁴⁷ has been unambiguously demonstrated by X-ray diffraction. Comparison of structures **307** and **308** revealed an intrachelate bond isomerism due to the ability of type **301** ligands to form metal-bridge fragments involving various donor atoms (X in compounds **308** or Y in compounds **307**).^{546,548}

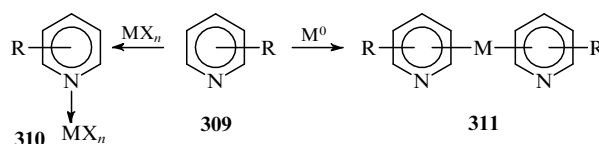
The dimeric complexes **307** possess antiferromagnetic properties (see, for example, Refs 541, 542, and 549). The magnetic behaviour of the dimeric compounds **308** should evidently be

similar. However, structures similar to that of compounds **308** have not been described for paramagnetic metals.

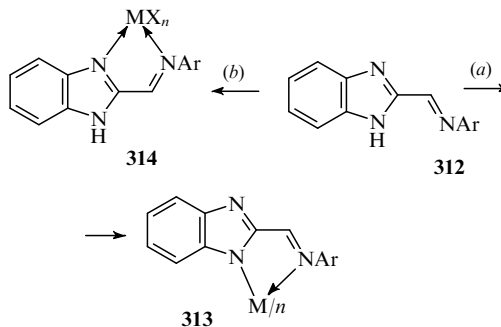
III. Regioselective synthesis. C-Metal-coordinated ligand systems

We consider regioselective synthesis from the standpoint of competitive coordination as a method for the preparation of complexes with a specified site (region) where the metal is bound to the ligand. Such synthesis may be based on allowance for the specificity of the soft–hard interactions.^{1–3,18} Thus hard and intermediate Pearson acids are used for the synthesis of complexes of the N-coordinated NCX group (X = S, Se),^{2,18} whereas complexes with the M–XCN fragment may be obtained mainly with participation of soft Pearson acids.^{2,18} A similar situation is observed also in the case of regioselective syntheses with participation of other ligands containing donor centres differing in hardness and softness: N, P; N, As; N, S; N, Se; N, Te; O, S; O, Se; O, Te.^{2,18}

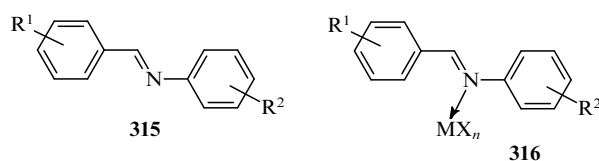
Specific regioselective complex formation is in many respects determined by the methods of synthesis of the coordination compounds. Thus, under the conditions of chemical synthesis from substituted pyridine derivatives **309**, the molecular adducts **310** are produced, whereas gas-phase synthesis^{299,300,550} opens a path to the π -complexes **311** of these ligands, which are difficult to obtain.

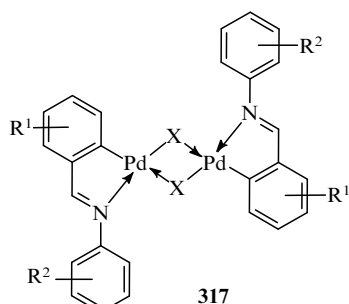


The use of electrosynthesis (path *a*)^{299,551} makes it possible to obtain the chelate complexes **313** from chelating ligands with weakly acid NH groups (for example, the azomethines **312**), whereas complexes **314** are formed¹ in the usual chemical syntheses (path *b*) (cf. Teom *et al.*⁵⁵²).



The cyclometallation^{553–558} and 1,3-dipolar cycloaddition^{559,560} reactions are used widely for the synthesis of metal complexes of azomethines, azo-compounds, and nitrogen-containing heterocycles with non-standard C-bonding of the ligands. Thus type **315** monodentate azomethines, which usually form $\eta^1(\text{N})$ -molecular adducts **316** with Lewis acids (MX_n), exhibit the properties of bidentate $\eta^2(\text{C},\text{N})$ -chelating ligands under the conditions of the cyclopalladation reaction and lead to chelate compounds,^{558,561} for example to compounds **317**.



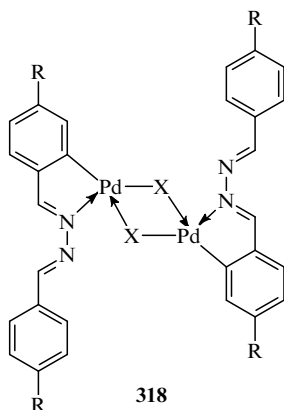


X = Cl, Br, SCN;

R¹, R² = H, Alk, OAlk, OCOAlk, Hal, CN, NO₂.

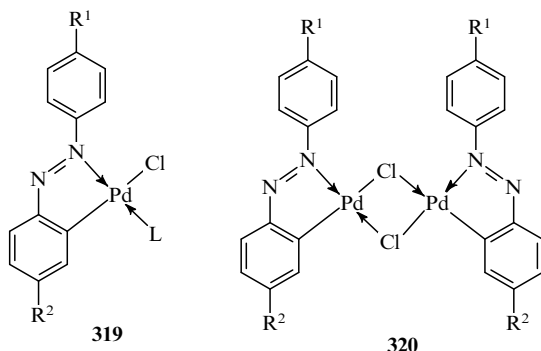
The formation of complex **317** (R¹ = 4-OMe, R² = 4-OBu) has been demonstrated by X-ray diffraction.⁵⁶¹

Cyclometallation, leading to a new Pd₄ cluster, is observed also in the acetolysis of bis(salicylaldiminato)palladium.⁵⁶² When the cyclometallation reaction is carried out with a series of aldazines,^{553, 555, 558, 563} chelates with C,N-coordinated ligands, for example complex **318**, are formed, as in the case of the azomethines considered above.



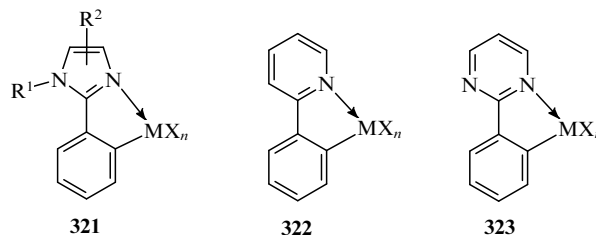
X = Cl, Br, NCS.

The same non-standard type of C,N-chelation occurs in cyclometallation reactions involving azo-compounds,^{358, 555, 556, 564} whereupon complexes **319** and **320** are formed.



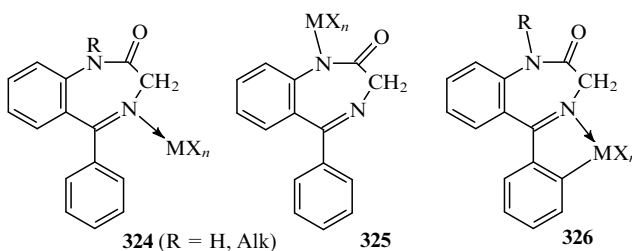
R¹, R² = Alk, OCOAlk; L = Py, quinoline.

We may also note the increase in denticity in the cyclometallation reactions of nitrogen-containing heterocycles: azoles, benzazoles (for example, compounds **321**),^{565, 566} and azines (for example, compounds **322** and **323**).^{553–558, 567–569}



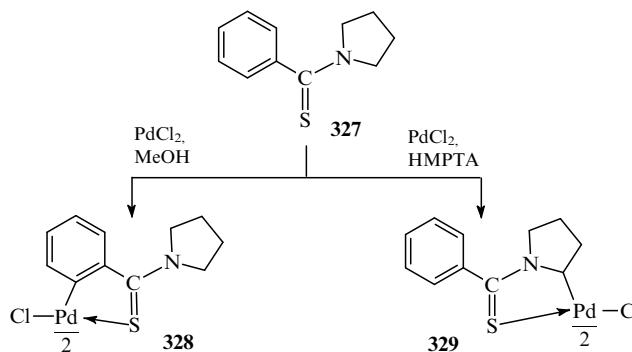
R¹ = H, Alk, Ar; R² = H, Alk, Ar, benzo.

Cyclometallation alters the location of the coordinate bond also in the series of complexes of more involved nitrogen-containing heterocycles, for example dibenzodiazepine derivatives (see Stoccoro *et al.*⁵⁷⁰ and the literature quoted therein). Thus 1,4-benzodiazepin-2-one usually affords adducts of types **324** and **325** on interaction with metal salts and organometallic compounds, whereas cyclometallation leads to the C,N-metal chelates **326**.⁵⁷⁰



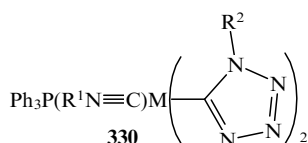
In a number of instances, the direction of coordination attack in regioselective synthesis is determined by the type of solvent. When aprotic solvents are employed, molecular adducts with a fully preserved ligand system may be obtained from typical chelating ligands (complexes **249–252** and **274**).^{22, 23, 503}

Other examples of the regulation of regioselective coordination by the type of solvent have been quoted in a review.⁵⁵⁶ In this connection, we may note the reaction



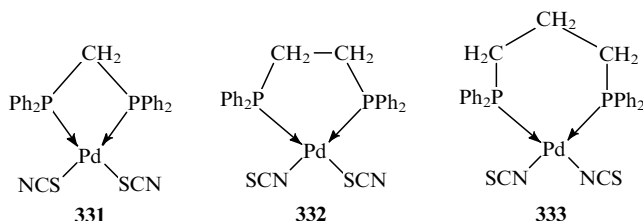
This regioselective synthesis, occurring in methanol or hexamethylphosphoramide (HMPA) with participation of N-thiobenzoylpyrrolidine **327**, is accompanied by the formation of two complexes, **328** and **329**, in which different cyclic systems are coordinated to the palladium atom. It is interesting because it demonstrates the possibility of the involvement in coordination of the S-donor ligand centre and of the saturated (and not aromatic or heterocyclic) CH fragment. We emphasise that the cyclometallation reactions can involve not only the C–H but also the C–Hal bonds.

Dipolar 1,3-cycloaddition^{16, 559} is interesting as regards the specific regioselective synthesis of a series of C-metal derivatives of nitrogen-containing heterocycles. The tetrazole derivatives **330** may be assigned to the latter.⁵⁵⁹



M = Hg, Pt, Pd.

The mode of the reactions in the regioselective synthesis depends on the fine structure of the ligand system, which has been demonstrated in relation to different types of coordination of the NCX group in palladium complexes of diphosphines with different lengths of the alkyl chain (complexes **331**–**333**).^{4, 31}



However, there are so far few examples of such regioselective reactions.

IV. Conclusion

The use of the concept of competitive coordination enabled us to survey extensive modern data concerning the regioselective binding of metals in complexes of bidentate and polydentate ligands. It is noteworthy that, in the majority of the publications which we have examined, only a particular mode of coordination was elucidated fairly reliably without analysis of the causes which would account for its regioselectivity. Nor is the situation saved by the application of the HSAB principle, since the latter can be used only for a limited range of ligands with soft and hard donor centres.

We believe that the main task in the development of the competitive coordination method is, firstly, the identification of the factors determining the centres at which the coordinate bond is located in complexes of bidentate and polydentate ligand systems. The solution of this problem will permit the specific regioselective synthesis of coordination compounds and will assist in studies devoted to the specific features of the binding of metals in biologically important systems.

The second task is the specific selection of ambident ligand systems with nitrogen–phosphorus and nitrogen–selenium (tellurium) donor centres and the synthesis from them of new metal complexes, the establishment of the structures of the latter, and the discovery of the causes of the regioselective coordination in these complexes. Despite the fact that continued interest has been shown in ligands of this type and the complexes obtained from them,^{77, 571–575} they still remain the least investigated objects in coordination chemistry.

In conclusion, one would wish to note that members of the Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences, the 80th Anniversary of which occurs next year, have made a major contribution to the development of the problem of the binding of metals in complexes of ambident ligands.

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Catalytic hydrogenation of thiolene 1,1-dioxides to thiolane 1,1-dioxide. Certain problems of the resistance of hydrogenation catalysts to sulfur

A V Mashkina

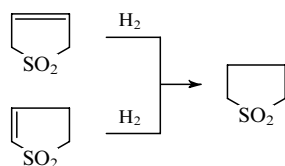
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Abstract. The state of research on the catalytic liquid-phase hydrogenation of 2- and 3-thiolene 1,1-dioxides to thiolane 1,1-dioxide is analysed. Data on the activities and selectivities of Group VIII metals and their complexes and sulfides, both massive and supported, as well as the reaction conditions and hydrogenation mechanisms are considered. The causes of the deactivation of catalysts in the synthesis of thiolane 1,1-dioxide and procedures for increasing their resistance to sulfur are described. Certain general problems of the resistance of hydrogenation catalysts to sulfur are discussed. The bibliography includes 130 references.

I. Introduction

Thiolane 1,1-dioxide, which has a series of valuable properties,¹ was first obtained in 1910 by the oxidation of thiolane.² However, a procedure proposed later^{3–5} and based on the reduction of 2- and 3-thiolene 1,1-dioxides by hydrogen in the presence of catalysts proved to be more convenient.



The initial compounds for the synthesis of thiolane 1,1-dioxide are fairly readily available: the interaction of buta-1,3-diene with sulfur dioxide affords a 95 mol. % yield of 3-thiolene 1,1-dioxide and isomerisation of the latter in a basic medium leads to 2-thiolene 1,1-dioxide in up to 60 mol. % yield.⁶

Nowadays, thiolane 1,1-dioxide is widely used as a reaction medium, as a plasticising and stabilising additive, as a component of hydraulic liquids, and as an anticorrosion additive to oils. It is also employed to purify resins and plant oils, to prepare a sulfur emulsion in water, etc. It is particularly important to note the use

of thiolane 1,1-dioxide as the extractant for the isolation of aromatic hydrocarbons from reformed petroleum products and as the solvent for the elimination of acid components from natural and industrial gases (see the relevant reviews^{1,7,8}). The need for this product stimulated the development of studies on the catalytic hydrogenation of thiolene 1,1-dioxides and led to the initiation of industrial production.^{7,9}

Up to the 1960s, information about the hydrogenation of thiolene 1,1-dioxides and thiolane 1,1-dioxide could be found only in the patent literature and a few research communications. Analysis of the results published at that time showed¹ that traditional low-temperature hydrogenation catalysts, such as platinum (platinum black and dioxide), palladium (palladium black and Pd/C), or nickel (Raney nickel and Ni/SiO₂) may be used for the hydrogenation of 2- and 3-thiolene 1,1-dioxides and their substituted derivatives to the corresponding thiolane 1,1-dioxide. The hydrogenation is usually carried out at 20–40 °C and atmospheric or reduced pressure in ethanol, isopropyl alcohol, water, acetic acid, dioxane, benzene, or thiolane 1,1-dioxide. The complete reduction of unsubstituted thiolene 1,1-dioxide in the presence of an excess of the catalyst relative to the substrate (34 mass %–250 mass %) requires several minutes, whereas in the presence of a low content of the catalyst (1 mass %–4 mass %) up to 20 h is required.

Various investigators studied the hydrogenation of thiolene 1,1-dioxides under different conditions. In a number of instances, the catalytic activity was determined without testing for the presence or absence of diffusional complications and without taking into account the surface area of the active component, which greatly hinders comparison of the results. Extensive experimental data have now accumulated. Nevertheless, important factors such as the dependence of the activity of the metal on its surface concentration on various carriers, the mechanism and kinetics of the hydrogenation reaction, and the resistance of the catalysts to sulfur have not been considered in detail in the very brief reviews available.^{10–14} It has therefore become necessary to analyse all the existing data and to determine the possible aspects of further research.

II. Hydrogenation of 2- and 3-thiolene 1,1-dioxides on massive and supported transition metal sulfides

Group VI–VIII metal sulfides are used as catalysts in the hydrogenation reactions of sulfur-containing raw material. They are not poisoned by sulfur compounds and exhibit an adequate activity at elevated temperatures and pressures and for prolonged contact

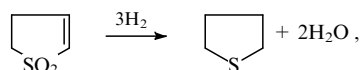
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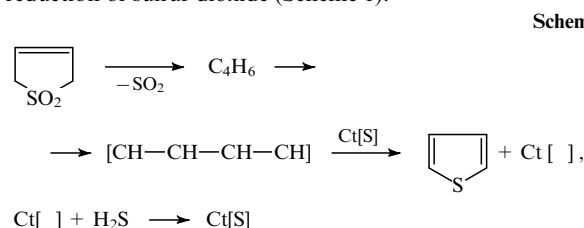
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times.¹⁵ Such severe conditions arise in the first place from the difficulty of activating hydrogen, which requires the transfer of its electrons to the acceptor centres, arising as a result of the displacement of electron density from the metal to the sulfur atom of the catalyst. The metal atoms in the sulfide are separated by sulfur atoms and this hinders the activation of unsaturated compounds which requires a structural correspondence.¹⁶

Molybdenum, tungsten, nickel, cobalt, and iron sulfides are not effective catalysts of the synthesis of thiolane 1,1-dioxide by the hydrogenation of thiolene 1,1-dioxides. Thus patent data (see the present author's earlier review¹) indicate that the hydrogenation of 2-thiolene 1,1-dioxide on these sulfides proceeds with formation of thiolane:



while thiophene is formed from 3-thiolene 1,1-dioxide (250–425 °C, 2–20 MPa). In the latter case, the 3-thiolene 1,3-dioxide formed probably decomposes to buta-1,3-diene and sulfur dioxide. The reaction is known to proceed at a high rate at temperatures above 100 °C.⁶ On metal sulfides at an elevated temperature, buta-1,3-diene is dehydrogenated with formation of the $-\text{CH}=\text{CH}-$ fragments, which interact with the catalyst sulfur atom to form thiophene. The loss of sulfur by the catalyst is made good by its interaction with the hydrogen sulfide formed on reduction of sulfur dioxide (Scheme 1):¹⁷



Ct = catalyst.

It has been demonstrated experimentally^{10–14, 18–22} that, at a lower temperature in the presence of certain transition metal sulfides, thiolene 1,1-dioxides are reduced to thiolane 1,1-dioxides (Table 1). The hydrogenation is carried out in the liquid phase in the presence of both massive and supported catalysts. The degree of conversion of the substrate, the yield of thiolane 1,1-dioxide, the selectivity (S), and the rate of formation of the dioxide (W), as well as the stability of the catalyst depend on the reaction conditions, namely on the nature of the solvent, temperature, hydrogen pressure (P), contact time (t), the initial thiolene 1,1-dioxide concentration (c), and the content of the catalyst in solution (g_{ct}).[†]

It follows from Table 1 that, in the hydrogenation of 3-thiolene 1,1-dioxide, dissolved in isopropyl alcohol, at an elevated temperature and pressure in the presence of $\gamma\text{-Al}_2\text{O}_3$ modified with 0.5 mass % of osmium, platinum, rhenium, or rhodium sulfides or 2.4 mass % of palladium sulfide, and also in the presence of the 5% $\text{RuS}_2/\text{SiO}_2$ catalyst, the yield of thiolane 1,1-dioxide does not exceed 1 mol. % with $S \leq 10\%$ and $W = 0.008\text{--}0.025 \text{ mmol h}^{-1} \text{ g}^{-1}$. On the catalyst obtained by depositing 20 mass % of Re_2S_7 on $\gamma\text{-Al}_2\text{O}_3$, the rate of reaction increases by an order of magnitude ($W = 0.25 \text{ mmol h}^{-1} \text{ g}^{-1}$)

[†] All the data presented below are expressed in identical units: the rate of reaction is expressed in moles of thiolane 1,1-dioxide formed per unit time on 1 g of the catalyst, on 1 g-atom of the metal, or on 1 m² of the surface of the active component; the stability of the catalyst is expressed in millimoles of thiolane 1,1-dioxide obtained during the period of the complete deactivation of 1 g of the catalyst or 1 m² of the metal; the content of the substrate in the solution hydrogenated is expressed on the molar scale and that of the catalyst in g litre^{−1}.

Table 1. Hydrogenation of 2- and 3-thiolene 1,1-dioxides on metal sulfides in isopropyl alcohol ($c = 0.25\text{--}0.4 \text{ M}$, $g_{\text{ct}} = 10 \text{ g litre}^{-1}$).^{18, 19}

Catalyst ^a	$T/^\circ\text{C}$	P/MPa	t/min	Yield of thiolane 1,1-dioxide (%)	$S(\%)$	W^b
3-Thiolene 1,1-dioxide						
Rh_2S_3 (9)	20	5	1	5	100	61.6
0.5% $\text{Rh}_2\text{S}_3/\text{Al}_2\text{O}_3$	100	25	420	1	10	0.025
PdS (6)	20	5	0.8	2.5	100	30.8
2.4% $\text{PdS}/\text{Al}_2\text{O}_3$	100	25	420	1	1	0.017
PtS_2 (66)	20	5	1	2	100	20.8
0.5% $\text{PtS}_2/\text{Al}_2\text{O}_3$	100	25	420	0.5	0.5	0.008
Re_2S_7 (9)	100	25	420	51	52	1.3
0.5% $\text{Re}_2\text{S}_7/\text{Al}_2\text{O}_3$	100	25	420	0.5	1	0.02
20% $\text{Re}_2\text{S}_7/\text{Al}_2\text{O}_3$	100	25	420	10	14	0.25
5% $\text{RuS}_2/\text{SiO}_2$	100	25	420	0.5	0.5	0.008
0.5% $\text{OsS}_2/\text{Al}_2\text{O}_3$	100	25	420	1	1	0.025
2-Thiolene 1,1-dioxide						
Rh_2S_3 (9)	150	11	60	90	90	22.5
0.5% $\text{Rh}_2\text{S}_3/\text{Al}_2\text{O}_3$	100	25	180	11	18	0.92
	150	25	180	28	28	2.33
PdS (6)	150	11	30	68	100	34.1
	150	11	60	84	88	21.0
0.5% $\text{PdS}/\text{Al}_2\text{O}_3$	150	25	180	77	77	6.4
2.4% $\text{PdS}/\text{Al}_2\text{O}_3$	150	25	180	68	68	5.7
4.7% $\text{PdS}/\text{Al}_2\text{O}_3$	150	11	60	30	100	7.5
Re_2S_7 (9)	150	11	60	48	72	12.0
0.5% $\text{Re}_2\text{S}_7/\text{Al}_2\text{O}_3$	150	25	180	67	67	0.02
20% $\text{Re}_2\text{S}_7/\text{Al}_2\text{O}_3$	100	25	420	49	50	1.8
PtS_2 (66)	150	16	60	47	68	11.7
0.5% $\text{PtS}_2/\text{Al}_2\text{O}_3$	100	25	420	9	10	0.22
OsS_2 (34)	150	11	60	78	88	19.6
0.5% $\text{OsS}_2/\text{Al}_2\text{O}_3$	150	25	180	7	10	0.6
5% $\text{RuS}_2/\text{SiO}_2$	100	25	420	16	34	0.42
WS_2 (11)	150	11	60	6	39	1.5
NiS (19)	150	11	60	3	46	0.83
CoS (9.5)	150	11	60	6	86	1.5

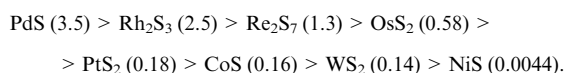
^a The values of S_{sp} expressed in m² g^{−1} are given in brackets. ^b Expressed in mmol h^{−1} g^{−1}.

and the yield of thiolane 1,1-dioxide is 10% for $S = 14\%$. When massive Re_2S_7 is used, the yield reaches more than 50% and $W = 1.3 \text{ mmol h}^{-1} \text{ g}^{-1}$. The unsatisfactory results can be explained by the decomposition of the unstable initial substrate under the conditions of a high temperature (100 °C) and a long contact time (7 h). Indeed, when the contact time is reduced to 1–2 h the hydrogenation of 3-thiolene 1,1-dioxide on the 2.5% $\text{PdS}/\text{Al}_2\text{O}_3$ catalyst in dilute solutions in methanol, butanol, and dimethylformamide leads to the formation of thiolane 1,1-dioxide in 50%–90% yield with $W = 0.42\text{--}0.85 \text{ mmol h}^{-1} \text{ g}^{-1}$ and $S \leq 90\%$ (100 °C, $P = 5 \text{ MPa}$, $c = 0.04 \text{ M}$, $g_{\text{ct}} = 50 \text{ g litre}^{-1}$).

A decrease in temperature to 20 °C induces a rise of the selectivity in the formation of thiolane 1,1-dioxide. Thus, in the hydrogenation of 3-thiolene 1,1-dioxide on massive platinum, palladium, or rhodium sulfides at $P = 5 \text{ MPa}$, the product yield is only 2%–5%, but $S = 100\%$ and $W = 21\text{--}62 \text{ mmol h}^{-1} \text{ g}^{-1}$.¹⁸ Under these conditions, the activity of rhodium sulfide calculated per gram of the massive catalyst is twice as high as that of palladium sulfide and three times as high as that of platinum sulfide (Table 1). The specific activities, calculated per unit area, of rhodium and palladium sulfides are approximately the same and exceed by more than an order of magnitude the specific activity of platinum sulfide (6.84, 5.13, and 0.32 mmol h^{−1} m^{−2} respectively).

In the hydrogenation of the thermally more stable 2-thiolene 1,1-dioxide on transition metal sulfides, satisfactory parameters likewise cannot be always attained.^{19,20} Thus in isopropyl alcohol the hydrogenation does not take place on massive V_2S_3 ($S = 7 \text{ m}^2 \text{ g}^{-1}$) and MnS ($S_{sp} = 2.3 \text{ m}^2 \text{ g}^{-1}$), whereas on tungsten, nickel, and cobalt sulfides the yield of thiolane 1,1-dioxide does not exceed 6% for a reaction rate of $1.5 \text{ mmol h}^{-1} \text{ g}^{-1}$. When massive rhenium, platinum, osmium, rhodium, or palladium sulfides are used as the catalyst, the yield of thiolane 1,1-dioxide reaches 50%–90% in 1 h, the selectivity is less than 100% owing to the partial decomposition of the substrate, and the rate of hydrogenation per gram of the catalyst exceeds by an order of magnitude the rate of reaction on tungsten, nickel, and cobalt sulfides ($W = 12\text{--}23 \text{ mmol h}^{-1} \text{ g}^{-1}$). However W decreases when the sulfides are deposited on Al_2O_3 or SiO_2 ($100\text{--}150^\circ\text{C}$, $P = 11\text{--}25 \text{ MPa}$, $c = 0.2\text{--}0.37 \text{ M}$) (Table 1).

In terms of their specific activity in the hydrogenation of 2-thiolene 1,1-dioxide at 150°C at $P = 11 \text{ MPa}$, the massive metal sulfides can be arranged in the following series (the values of W expressed in $\text{mmol h}^{-1} \text{ m}^{-2}$ are given in brackets):



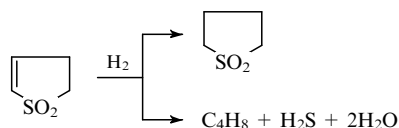
Nickel sulfide has the lowest specific activity, while platinum, rhenium, cobalt, and tungsten sulfides are approximately four times more active and rhodium and palladium sulfides are up to 60–80 times more active than nickel sulfide. Under the same conditions, the greatest selectivity in the formation of thiolane 1,1-dioxide is obtained on massive rhodium, palladium, osmium, and cobalt sulfides ($S \approx 90\%$). It is somewhat lower on rhenium and platinum sulfides ($S \approx 70\%$), and is especially low on tungsten and nickel sulfides ($S < 50\%$).

The hydrogenation of 2-thiolene 1,1-dioxide has been investigated in greater detail on palladium sulfide, 0.5 mass %–7.6 mass % of which had been deposited on $\gamma\text{-Al}_2\text{O}_3$.^{11,19}

In the presence of 0.5% $\text{PdS}/\text{Al}_2\text{O}_3$, an increase in temperature from 50 to 200°C with the remaining parameters unaltered leads to an increase in the yield of thiolane 1,1-dioxide from 14% to 70% for $S = 70\%$ ($P = 25 \text{ MPa}$, $c = 0.26 \text{ M}$, $g_{ct} = 10 \text{ g litre}^{-1}$, $t = 7 \text{ h}$). On the 4.7% $\text{PdS}/\text{Al}_2\text{O}_3$ catalyst, such an increase in temperature induces an increase in yield from 5% to 36% for $S = 100\%$ ($P = 11 \text{ MPa}$, $c = 0.21 \text{ M}$, $g_{ct} = 10 \text{ g litre}^{-1}$, $t = 1 \text{ h}$).

On the 2.4% $\text{PdS}/\text{Al}_2\text{O}_3$ catalyst at 150°C , $P = 25 \text{ MPa}$, and $g_{ct} = 10 \text{ g litre}^{-1}$, the degree of conversion of 2-thiolene 1,1-dioxide is independent of its initial concentration in the range from 0.02 to 0.12 M, while the rate of hydrogenation is proportional to the concentration of the substrate. The rate of reaction at $c = 0.37 \text{ M}$ is proportional to the hydrogen pressure in the range from 1 to 15 MPa. For higher values of c and P , the rate ceases to change, i.e. the reaction is of zero order with respect to 2-thiolene 1,1-dioxide and hydrogen.

On the 2.4% $\text{PdS}/\text{Al}_2\text{O}_3$ catalyst, the degree of conversion of 2-thiolene 1,1-dioxide dissolved in isopropyl alcohol may attain 100%, but the yield of thiolane 1,1-dioxide does not then exceed 70% (150°C , $P = 25 \text{ MPa}$, $c = 0.37 \text{ M}$, $g_{ct} = 10 \text{ g litre}^{-1}$), since hydrogenolysis products are formed together with thiolane 1,1-dioxide. The degree of conversion does not affect the selectivity. On the basis of these data, it was concluded¹⁹ that the initial 2-thiolene 1,1-dioxide, and not its hydrogenation product, undergoes hydrogenolysis, i.e. the hydrogenation and hydrogenolysis reactions proceed independently.



The $\text{PdS}/\text{Al}_2\text{O}_3$ catalyst is stable under the conditions of the hydrogenation of 2-thiolene 1,1-dioxides even after the formation

of $\sim 415 \text{ mmol}$ of thiolane 1,1-dioxide on 1 g of the catalyst, the rate of reaction remains unchanged.

III. The activities and stabilities of metal complexes in the hydrogenation reactions of 2- and 3-thiolene 1,1-dioxides

Metal complexes are promising catalysts for the reduction of various unsaturated compounds.²³ Certain platinum, palladium, and rhodium complexes exhibit an enhanced resistance to sulfur.^{24–29} The use of Group VIII metal complexes for the hydrogenation of 2- and 3-thiolene 1,1-dioxides has so far been investigated in insufficient detail.

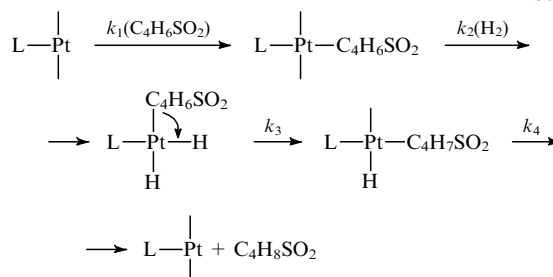
Rhodium complexes. In the hydrogenation of 3-thiolene 1,1-dioxide in the presence of tris(*tert*-phosphine)- or tris(*tert*-arsine)-rhodium nitrosyl complexes, a quantitative yield of thiolane 1,1-dioxide is attained after 16 h at 56°C and $P = 4 \text{ MPa}$.³⁰

Nickel complexes. In the presence of nickel acetylacetonate in solution in benzene to which aluminium isobutoxide has been added at a concentration of 31.6 M, exhaustive hydrogenation of 3-thiolene 1,1-dioxide takes place (25°C , $P = 1.4 \text{ MPa}$, $c = 1.8 \text{ M}$, $g_{ct} = 5.3 \text{ mmol litre}^{-1}$, $t = 35 \text{ min}$).³¹ The rate of formation of thiolane 1,1-dioxide per gram-atom of nickel is 576 mol h^{-1} .

Platinum complexes. In the presence of the complex $\text{PtCl}_2(\text{H}_2\text{O})[\text{P}(\text{C}_6\text{F}_5)_3]$ reduced by hydrogen, 3-thiolene 1,1-dioxide, dissolved in butanol, is hydrogenated to thiolane 1,1-dioxide in a yield of about 100%.³² The isomerisation of the initial substrate to 2-thiolene 1,1-dioxide also takes place to a slight extent (0.5%) (25°C , $P = 0.1 \text{ MPa}$, $c = 0.12 \text{ M}$, concentration of the complex 0.01 M , $t = 1.5 \text{ h}$). The rate of hydrogenation is $11.4 \text{ mol h}^{-1} (\text{g-atom Pt})^{-1}$. A kinetic study showed³³ that the order of this reaction with respect to platinum at a platinum concentration in the range $[\text{Pt}] = (2.5\text{--}10) \times 10^{-3} \text{ M}$ is unity. Hence it was concluded that the catalyst contains no ligands capable of splitting off from the initial complex under the influence of the solvent. The rate of hydrogenation at $c < 0.01 \text{ M}$ increases with increase in the 3-thiolene 1,1-dioxide concentration raised to a power of 0.55, whilst at $c = 0.05\text{--}0.1 \text{ M}$ it remains unchanged. The order of the reaction with respect to hydrogen at pressures close to atmospheric is zero, whilst at low partial pressures ($\sim 0.006 \text{ MPa}$) it increases to 0.7. In the temperature range from 0 to 62.5°C , the activation energy for the reaction is 46 kJ mol^{-1} .

It has been suggested³³ that the reaction proceeds *via* consecutive stages involving coordination to the complex of 3-thiolene 1,1-dioxide and hydrogen and the formation of a hydride complex and its decomposition (Scheme 2).

Scheme 2



Here L is the stabilising ligand in the reduced platinum complex formed from $\text{P}(\text{C}_6\text{F}_5)_3$, while $k_1\text{--}k_4$ are the rate constants for the corresponding stages. The rate of reaction is limited by the formation of the hydride complex (stage 3) and is described by the equation

$$W = \frac{k_3 K_1 K_2 c_1 c_2 c_3}{1 + K_1 c_2 + K_1 K_2 c_2 c_3},$$

where K_1 and K_2 are the equilibrium constants of stages 1 and 2, c_1 is the overall concentration of the complexes formed in all the reaction stages, c_2 is the concentration of 3-thiolene 1,1-dioxide, and c_3 is the concentration of hydrogen in solution, equal to P_{H_2} multiplied by the solubility coefficient of the gas.

At a high substrate concentration, the equation becomes

$$W = \frac{k_3 K_2 c_1 c_3}{1 + k_2 c_3},$$

and at a high hydrogen concentration it assumes the form

$$W = k_3 c_1.$$

These equations agree with experimental data.

On consecutive hydrogenation of several portions of 3-thiolene 1,1-dioxide in the same contact solution, the reaction rate diminishes from experiment to experiment. After the formation of 100 mmol of thiolane 1,1-dioxide per mg-atom of platinum, the initial activity becomes smaller by a factor of two. It can also be postulated that the deactivation of the platinum complex is associated with the formation of small amounts of buta-1,3-diene and sulfur dioxide on decomposition of the substrate. However, the addition of buta-1,3-diene at a concentration of $(3.3 - 16.7) \times 10^{-3}$ M did not decrease but actually increased the activity of the catalyst by a factor of 1.3–3. On the other hand, sulfur dioxide is a poison for the platinum complex, its introduction into the solution hydrogenated at a concentration of 1.2×10^{-3} M (molar ratio $SO_2 : Pt = 0.1$) reduces the initial activity of the catalyst approximately by a factor of 80. In the presence of the above platinum complex, SO_2 is not reduced to hydrogen sulfide even after 3.5 h and it was therefore concluded³² that the poison for the catalyst considered is sulfur dioxide itself.

Homogeneous palladium complexes. The hydrogenation of 2-thiolene 1,1-dioxide has been investigated³⁴ in the presence of palladium complexes with sulfur- and nitrogen-containing ligands in solution in dimethyl sulfoxide. The potassium tetrahydroborate-reduced palladium complexes of dimethyl sulfide and dimethyl sulfoxide, $PdCl_2 \cdot (DMS)_2 \cdot KBH_4$ and $PdCl_2 \cdot (DMSO)_2 \cdot KBH_4$, in which the degree of oxidation of palladium is reduced, accelerate the hydrogenation of 2-thiolene 1,1-dioxide. The reaction proceeds at a high rate $W = 1 \text{ mol min}^{-1} (\text{g-atom Pd})^{-1}$ (20°C , $P = 0.1 \text{ MPa}$, $c = 0.127 \text{ M}$). The analogous palladium complexes of diethyl sulfide or thiolane are less active [$W = 0.06$ and $0.03 \text{ mol min}^{-1} (\text{g-atom Pd})^{-1}$ respectively] and decompose under the influence of the reaction medium with liberation of metallic palladium.

The homogeneous palladium complex of dimethylformamide ($PdCl_2 \cdot DMF$) proved to be approximately 45 times more active than the complexes with sulfur-containing ligands.

However, the addition of divalent sulfur compounds reduces the initial activity of the homogeneous palladium complexes. Thus, when thiophene or thiolane were added to the hydrogenated solution at a concentration of 50×10^{-3} M, the activity of the palladium complex of dimethyl sulfide diminished by a factor of 2 and the complex decomposed with liberation of metallic palladium. In order to poison the palladium complex of dimethyl sulfoxide to the same extent, it is necessary to introduce ten times more of thiolane to the hydrogenated solution. This can be accounted for by the difficulty of the incorporation of thiolane in the coordination sphere of the palladium complex, since palladium forms bonds with the sulfur and oxygen atoms of dimethyl sulfoxide.

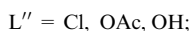
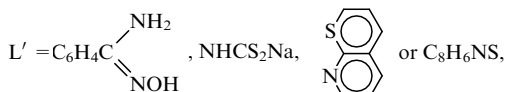
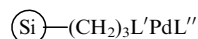
The activity of the complex $PdCl_2 \cdot DMF$ diminishes by a factor of 2 after the introduction into the solution of thiophene at a concentration of 60×10^{-3} M or thiolane at a concentration of 0.3×10^{-3} M. Such a high difference between the toxicities can be accounted for by the fact that dimethylformamide, which is a stronger electron donor, can compete with thiophene for coordination to palladium, whereas thiolane substitutes dimethylformamide in the coordination sphere of palladium, forming a complex

with the latter. The complex is unstable in a reducing medium and decomposes to metallic palladium, which is readily deactivated (see Section V). In terms of resistance to poisoning by thiolane, $PdCl_2 \cdot DMF$ is inferior to palladium complexes with sulfur-containing ligands by 2–3 orders of magnitude.

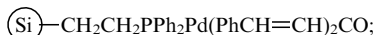
The cause of the deactivation of homogeneous palladium complexes has been investigated³⁴ by UV and NMR spectroscopy. Absorption bands characteristic of the $Pd^{2+} - S$ bond (26 000 and 34 000 cm) appear in the UV spectrum of the complex partly deactivated by the addition of $(5 - 10) \times 10^{-3}$ M thiolane (poison : Pd = 2–5). At a thiolane concentration of 50×10^{-3} M (poison : Pd = 50), all the absorption bands vanish from the spectrum, which indicates the decomposition of the complex.

The ^{13}C NMR spectra of a $PdCl_2 \cdot (DMS)_2 \cdot KBH_4$ specimen to which small amounts of thiolane have been added exhibit signals belonging to thiolane coordinated to palladium ($\delta = 40.3$ and 32.8 ppm) and to free dimethyl sulfide ($\delta = 20.6$ ppm). On this basis, it was concluded that deactivation occurs as a result of the displacement by thiolane of the initial ligand from the coordination sphere of the complex and the disruption of the initial structure of the latter. In hydrogen, the newly formed complex decomposes with liberation of metallic palladium, which is readily poisoned by sulfur compounds.

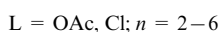
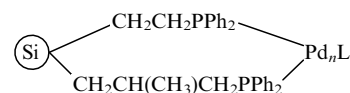
Heterogenised palladium complexes. The hydrogenation of 2- and 3-thiolene 1,1-dioxides on mononuclear and polynuclear Pd^{2+} and Pd^0 complexes immobilised on silicon dioxide has been investigated.^{34–38} These complexes include the mononuclear Pd^{2+} complexes



the mononuclear Pd^0 complex



and polynuclear complexes of the type



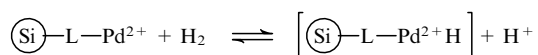
or



In the presence of heterogenised complexes in methanol and isopropyl alcohol, thiolene 1,1-dioxides are fully reduced to thiolane 1,1-dioxide (20°C , $P = 0.1 \text{ MPa}$, $c = 0.127 \text{ M}$, $g_{\text{ct}} = 1.5 - 10 \text{ g litre}^{-1}$). Depending on the composition of the complex, the rate of hydrogenation ranges from 1 to $90 \text{ mol min}^{-1} (\text{g-atom Pd})^{-1}$ (Refs 35, 36), i.e. has the same order of magnitude as on the homogeneous complex $PdCl_2 \cdot DMF$ and on supported metallic palladium (0.2 mass %–5 mass %).³⁴

The catalytic activity of mononuclear Pd^{2+} complexes increases with increase in the instability constant of the complex.³⁵ The hydrogenation reaction must involve the coordination of thiolene 1,1-dioxide with formation of a π -complex and the activation of hydrogen *via* the formation of palladium hydride. Palladium hydride is formed on the Pd^{2+} complex on transfer of electron density from hydrogen to palladium.²⁹ It has been suggested^{37,38} that the rate-limiting stage of the hydrogenation of thiolene 1,1-dioxide on Pd^{2+} complexes is the activation of hydrogen. After the enhancement of the electron-donating prop-

erties of the ligands, the instability constant decreases. This shifts the equilibrium



towards a decrease in the concentration of palladium hydride and hence leads to a decrease in the rate of hydrogenation.

Polynuclear diphosphine Pd^0 complexes, immobilised on silicon dioxide, are somewhat less active than the mononuclear complexes. Their activity increases with increase in the number of palladium atoms from 2 to 6. The monophosphine Pd^0 complex is the most active. The rate of reaction on this complex reaches $92 \text{ mol min}^{-1} (\text{mol Pd})^{-1}$, which can be accounted for by its conversion under the hydrogenation conditions into the coordinatively unsaturated immobilised complex $(\text{Si})-(\text{CH}_2)_2\text{PPh}_2\text{Pd}^0$, which activates hydrogen and multiple bonds more readily.²⁹

In the course of one experiment, the activity of the heterogenised complex does not change, but, after prolonged hydrogenation of 2- and 3-thiolene 1,1-dioxides, a slow deactivation of the catalyst is observed. It is probably caused by the effect of the divalent and tetravalent sulfur compounds formed. The resistance of the complexes to sulfur was determined by adding thiolane and thiophene to the hydrogenated solution.^{34–38} It was found that the resistances of the mononuclear Pd^{2+} and polynuclear Pd^0 complexes to poisoning by the above substances are approximately the same. The immobilised palladium complexes with nitrogen-containing ligands are 40–500 times less resistant to poisoning by thiolane and thiophene than the homogeneous palladium complex of dimethylformamide.³⁴

The causes of the deactivation of the heterogenised palladium complexes by thiolane and thiophene have been investigated.^{13, 34–38} Thiolane is a stronger poison than thiophene adsorption measurements have shown that the formation constant of the thiophene–catalyst complex is three times smaller than the corresponding constant for the thiolane–catalyst complex. It follows from desorption experiments that the deactivation by thiophene is partly reversible, whilst thiolane poisons the complex irreversibly. In dimethylformamide, which is an effective complex-forming agent and competes with the sulfur-containing poison, the resistance of the complex to poisoning is greater than in isopropyl alcohol (for the ratio poison: Pd = 100:1). The stability of the mononuclear Pd^{2+} complexes depends on the electron-donating capacity of the inner ligands, characterised by the instability constant of the complex with decrease in the latter, the strength of the $(\text{Si})-\text{L}-\text{Pd}$ linkage increases, while the ability of palladium to be coordinated to the poison $(\text{Si})-\text{L}-\text{Pd} \leftarrow \text{S} <$ diminishes. The stability of the polynuclear complexes is determined both by the strength of the bond between palladium and the inner ligand and by steric factors. The role of the latter increases with increase in nuclearity. Owing to the small size of the framework of the cluster, not all the palladium atoms are sterically capable of forming bonds with the molecules of the poison, but they can activate hydrogen.

According to XPS data, the mononuclear Pd^{2+} complexes change after treatment with thiolane. In the $\text{Pd}3d$ spectral range, the binding energy diminishes from 337.2 to 336.7 eV for $B = 3.4\text{--}3.5 \text{ eV}$, which indicates a decrease in the valence of palladium. The intensity of the $\text{Pd}3d/\text{Si}3p$ lines then decreases slightly (from 0.23 to 0.21). In the region of $\text{S}2p$ and $\text{S}2s$, sulfur lines were observed. A shoulder appears in the UV spectrum of the specimen treated with the poison in the range $34\,000\text{--}24\,000 \text{ cm}^{-1}$, which corresponds to the bond between Pd^{2+} and sulfur. The XPS spectra of the initial Pd^0 complex and the same complex treated with thiolane are characterised by a constant binding energy (336.1 eV) and line half-width (4.4–4.1 eV). The decrease after the treatment of the catalyst in the intensity of the $\text{Pd}3d/\text{Si}2p$ lines from 0.36 to 0.26 can be explained by the shielding of the palladium signal by the adsorbed molecules of the poison.

Analysis of the UV spectra also indicates the preservation of the structure of the complex when it is treated with thiolane

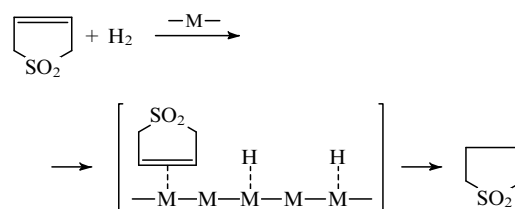
(absorption bands at $28\,000$, $22\,000$, and $16\,000 \text{ cm}^{-1}$). Treatment with a large amount of the poison at an elevated temperature induces the decomposition of the initial structure of the complex, which is indicated by the decrease in the binding energy, the line half-width, and the intensity of the signals in the XPS spectrum and also by the disappearance from the UV spectrum of the bands characteristic of the initial complex. It may be that the decomposition of the complex is accompanied by the formation of the $\text{Pd} \leftarrow \text{S} <$ bond. Thus the deactivation of the palladium complexes immobilised on silicon dioxide takes place as a consequence of the displacement of the outer ligand by the sulfur poison entering into the coordination sphere of palladium and of the formation of a bond between palladium and sulfur. Under certain conditions, the structure of the complex is fully disintegrated.

IV. The activities of massive and supported metals in the hydrogenation reactions of thiolene 1,1-dioxides

Group VIII metals are used widely for the low-temperature hydrogenation of various unsaturated organic compounds.^{17, 39}

The multiple bond in thiolene 1,1-dioxides is activated by virtue of the presence of the electron-accepting sulfonyl group.^{6, 40} This facilitates the formation of a complex with participation of the $\text{C}=\text{C}$ bond, which may become saturated in the presence of activated hydrogen in the system (Scheme 3).

Scheme 3



The reaction mechanism involves the postulate that the unsaturated organic substrate and hydrogen are activated on different active centres as a result of the transfer of electron density from the occupied atomic orbital of the metal to the $\text{C}=\text{C}$ bond and to the unoccupied antibonding molecular orbitals of hydrogen.^{17, 39, 41} This is to some extent confirmed, particularly by the results of experiments involving the introduction into the reaction mixtures of additives competing with the reactants for the formation of bonds with the metal. Thus, in the interaction of sulfur dioxide — a strong electron acceptor⁴⁰ — with the metal, electrons are transferred to the d orbital of the sulfur atom and this prevents the formation of a π -olefin complex by the metal. Hydrogen sulfide forms a coordinate bond as a result of the transfer of the lone pair of sulfur to the unoccupied orbital of the metal, which ultimately leads to the formation of a surface metal sulfide, which poorly activates hydrogen.¹⁵

It has been shown in a series of studies that 2- and 3-thiolene 1,1-dioxides are hydrogenated on Group VIII metals under mild conditions to thiolane 1,1-dioxide with 100% selectivity.^{10–14, 42} More studies have been devoted to the reaction involving 3-thiolene 1,1-dioxide than to the reaction in which 2-thiolene 1,1-dioxide is hydrogenated because of the relative availabilities of the two dioxides. However, 3-thiolene 1,1-dioxide readily dissociates to buta-1,3-diene and sulfur dioxide. Its vigorous decomposition begins above 100°C , but it decomposes partly even at room temperature. 3-Thiolene 1,1-dioxide therefore always contains a certain amount of sulfur dioxide, which has a definite effect on the catalytic properties of metals. 2-Thiolene 1,1-dioxide is free of this disadvantage because it is thermally more stable.⁶

The hydrogenation of thiolene 1,1-dioxides on Group VIII metals is carried out in solutions at a low temperature and atmospheric or elevated pressure. The liquid-phase hydrogenation of 3-thiolene 1,1-dioxide has been studied in greatest detail on

metallic rhodium, nickel, and palladium, and in much smaller detail on osmium, iridium, ruthenium, and platinum. The results obtained on hydrogenation of thiolene 1,1-dioxides in the presence of Group VIII metals are examined below.

Iridium and osmium. The hydrogenation of 3-thiolene 1,1-dioxide on iridium and osmium has been investigated at 20 °C and $P = 5$ MPa in isopropyl alcohol to which 10 mass % of thiolane 1,1-dioxide had been added (Table 2).⁴² In the presence of iridium black, exhaustive reduction of 3-thiolene 1,1-dioxide took place in 5 min ($g_{ct} = 10.7$ g litre⁻¹, $[SO_2] < 0.03 \times 10^{-3}$ M). The initial rate of reaction in the kinetic region (for 20% conversion) was 0.39 mol h⁻¹ g⁻¹. Iridium, deposited in an amount of 1 mass %–2 mass % on γ -Al₂O₃, exhibited a somewhat higher activity than iridium black ($W = 0.5$ mol h⁻¹ g⁻¹). It may be that the degree of dispersion of iridium in the supported catalyst is somewhat greater, since the rate constant on the supported metal, referred to its unit surface, agrees with the value found for iridium black.

The 1.8 mass % Os/ γ -Al₂O₃ catalyst has a lower activity than the iridium catalyst; for $g_{ct} = 21.5$ g litre⁻¹, complete reduction

Table 2. The activities and stabilities of osmium, iridium, ruthenium, and platinum catalysts in the hydrogenation of 3-thiolene 1,1-dioxide (20 °C, $P = 5$ MPa, $c = 0.4$ M, solvent — isopropyl alcohol to which 10% of thiolane 1,1-dioxide has been added).⁴²

Catalyst	S_{sp}^a /m ² g ⁻¹	Activity ^b		Stability	
		see ^c	see ^d	mmol g ⁻¹	mmol m ⁻²
1.8% Os/Al ₂ O ₃	—	0.8	—	8.3	—
Ir	4	8.3	2.1	28	6.7
1% Ir/Al ₂ O ₃	200	5.6	2.8	17	8.3
1.9% Ir/Al ₂ O ₃	210	11.2	2.8	33	8.3
Ru	8	8.3	1.0	24	3.3
1% Ru/Al ₂ O ₃	250	2.5	1.0	8	4.2
2% Ru/Al ₂ O ₃	200	4.4	1.1	15	3.3
Pt	2.2	44	19	44	20
	88	1377	18	—	—
0.6% Pt/Al ₂ O ₃	267	29	18	33	21
2% Pt/Al ₂ O ₃	100	32	17	33	17

^a Specific surface calculated per unit mass of the metal. ^b The activity given in this and subsequent tables represents the rate constant. It was determined to within ± 10 rel. % per unit surface of the metal. ^c Expressed in mol h⁻¹ g⁻¹. ^d Expressed in mol h⁻¹ m⁻².

of 3-thiolene 1,1-dioxide is attained after 30 min ($W = 0.04$ mol h⁻¹ g⁻¹).

The rate of hydrogenation on iridium is proportional to the concentration of 3-thiolene 1,1-dioxide (at $c = 0.07$ –0.6 M) and the hydrogen pressure (at $P = 0.1$ –2 MPa). In the range of higher values of the above parameters, the rate of reaction remains unchanged.

Ruthenium. The activity of ruthenium in the hydrogenation of 3-thiolene 1,1-dioxide is close to that of iridium (Table 2). On ruthenium black, the 100% yield of thiolane 1,1-dioxide is attained after 6 min at the reaction rate in the kinetic region $W = 0.4$ mol h⁻¹ g⁻¹ ($c = 0.36$ M, $g_{ct} = 10.7$ g litre⁻¹, $[SO_2] < 0.03 \times 10^{-3}$ M).⁴² Under the same conditions, the rate of hydrogenation on supported ruthenium (1 mass %–2 mass % of Ru on γ -Al₂O₃) is 0.1–0.2 mol h⁻¹ g⁻¹. The specific activities of ruthenium on a carrier and of ruthenium black are the same (Table 2). However, if the hydrogenation of 3-thiolene 1,1-dioxide takes place under the conditions of diffusional complications (large catalyst grains, inadequate stirring of the mixture), the supported ruthenium catalyst exhibits a reduced activity:⁴³ exhaustive hydrogenation of 3-thiolene 1,1-dioxide in isopropyl alcohol is attained on this catalyst only after 0.5–1 h {20 °C,

$P = 0.1$ –10 MPa, $c = 0.2$ M, $g_{ct} = 9$ –18 g litre⁻¹, $[SO_2] < 0.03 \times 10^{-3}$ M}.

The activity of supported catalysts can be influenced by the chemical composition of the initial ruthenium compounds, which were potassium ruthenate and ruthenium chloride subjected to successive reduction with hydrogen at 300 °C. At atmospheric pressure, the activity of the catalyst prepared by depositing on charcoal the ruthenium obtained from potassium ruthenate was higher than the activity of the catalyst obtained from ruthenium trichloride. On the other hand, the aluminoruthenium catalysts obtained from potassium ruthenate and ruthenium trichloride have approximately the same activities. The catalyst on silicon dioxide, obtained by depositing ruthenium obtained from the trichloride, is appreciably more active than the specimen prepared from potassium ruthenate.

When the same initial ruthenium compound is used, the catalytic activity is influenced by the nature of the carrier. Thus the activities of the catalyst on γ -Al₂O₃ and activated charcoal are an order of magnitude higher than the activity of ruthenium on silicon dioxide. It has been suggested⁴³ that this is caused by the different degrees of dispersion of ruthenium and the different chemical compositions of the active component, which consists of a mixture of metallic ruthenium and its oxide, the activities of which differ by a factor of 2.⁴²

When 5 mass % of ruthenium is deposited on the Ni/Cr₂O₃ or Ni/SiO₂ industrial nickel catalyst, the activity of the latter either does not change or decreases. On the other hand, the introduction of 5 mass % of ruthenium (obtained from ruthenium trichloride) into an industrial aluminoplatinum catalyst increases its activity by a factor of 2.⁴³

A kinetic study showed⁴² that at $P < 2$ MPa the rate of hydrogenation is proportional to the hydrogen pressure and is independent of the concentration of the substrate. The process is apparently limited by the activation of hydrogen. When 3-thiolene 1,1-dioxide is introduced into a hydrogenated solution containing the hydrogen-saturated 5% Ru/Al₂O₃ catalyst, the potential undergoes a very marked shift to the anodic region (by 600–700 mV), which indicates a significant displacement of hydrogen from the surface by the substrate. An increase in pressure to 2–5 MPa alters the mechanism of the reaction, its rate at 20 °C becomes proportional to the concentration of 3-thiolene 1,1-dioxide (at $c = 0.07$ –0.7 M), but is independent of hydrogen pressure.

Platinum. The hydrogenation of 3-thiolene 1,1-dioxide on supported platinum catalysts is slow.^{44,45} In ethanol on the 4.8 mass % Pt/C catalyst, the yield of thiolane 1,1-dioxide was 81% with $W = 0.017$ mol h⁻¹ g⁻¹ (20 °C, $P = 0.1$ MPa, $c = 0.35$ M, $g_{ct} = 4.8$ g litre⁻¹, $t = 3.5$ h).⁴⁴ The industrial aluminoplatinum catalyst AP-56 also exhibited a low activity in isopropyl alcohol. The rate of reaction on this catalyst was 0.08 mol h⁻¹ g⁻¹ (20 °C, $P = 0.1$ MPa, $c = 0.4$ M, $g_{ct} = 20$ g litre⁻¹).⁴⁶ However, according to other data, catalysts containing 0.6 and 2 mass % of Pt on γ -Al₂O₃ have a much higher activity in isopropyl alcohol to which 10 mass % of thiolane 1,1-dioxide has been added. On these catalysts, $W = 1.1$ –1.2 mol h⁻¹ g⁻¹ {20 °C, $P = 5$ MPa, $c = 0.4$ M, $[SO_2] < 0.03 \times 10^{-3}$ M}.⁴² This discrepancy can apparently be accounted for by the fact that Mashkina *et al.*⁴² hydrogenated a substrate from which sulfur dioxide had been thoroughly removed and carried out the reaction in the absence of diffusional complications, whereas these conditions were not maintained in the studies of Virobyants and coworkers.^{44,45} In the hydrogenation of 3-thiolene 1,1-dioxide on platinum black under thoroughly controlled conditions, the 100% yield of thiolene 1,1-dioxide was attained after 1.5 min with $W = 1.5$ mol h⁻¹ g⁻¹ (20 °C, $P = 5$ MPa, $c = 0.37$ M, $g_{ct} = 10.7$ g litre⁻¹).⁴² In the presence of platinum obtained by the reduction of its dioxide, the rate of hydrogenation per unit mass of the catalyst increases under the conditions indicated by a factor of 32, which can be explained by the increase in the specific surface of the metal. The activities of massive

platinum and platinum deposited on γ - Al_2O_3 , calculated per unit surface, are the same (Table 2).

The rate of hydrogenation on platinum black at 20 °C in isopropyl alcohol to which 10 mass % of thiolane 1,1-dioxide has been added is proportional to the concentration of 3-thiolene 1,1-dioxide ($P = 5$ MPa, $c = 0.05$ – 0.6 M) and the hydrogen pressure ($c = 0.4$ M, $P = 0.1$ – 2 MPa).⁴² At $P > 2$ MPa, the rate of reaction ceases to depend on the pressure. At atmospheric pressure on platinum black in ethanol, the reaction was found to be of first order with respect to 3-thiolene 1,1-dioxide (30–45 °C, $c = 0.077$ M). The increase in the rate of hydrogenation with increase in temperature is characterised by an activation energy of 22 kJ mol⁻¹.

The ratio of the concentrations of the reactants on the surface of the platinum catalyst was estimated in the course of the process by measuring the catalyst potential.⁴⁷ The reversible hydrogen potential of platinum, which is 600–660 mV, shifted by only 50 mV during the hydrogenation reaction. This permitted the conclusion that most of the catalyst surface is occupied by hydrogen and that the rate of reaction is limited by the activation of 3-thiolene 1,1-dioxide. In 0.1 N alcoholic solution of hydrochloric acid, the rate of hydrogenation is approximately twice as high as in a neutral medium and the reaction order with respect to thiophene 1,1-dioxide approaches zero.

Rhodium. Metallic rhodium exhibits a very high activity in the hydrogenation of 3-thiolene 1,1-dioxide.^{42, 48–50} In isopropyl alcohol to which 10 mass % of thiolane 1,1-dioxide has been added, exhaustive hydrogenation is attained on rhodium black after 0.5 min with $W = 54$ mol h⁻¹ g⁻¹ (at 20 °C $P = 5$ MPa, $c = 0.37$ M, $g_{\text{ct}} = 8.6$ g litre⁻¹).⁴⁸ When rhodium is deposited on a carrier, its activity becomes even higher. This can be explained by the increase in the degree of dispersion of the metal, which has been confirmed by data on the chemisorption of oxygen.⁵¹ The degree of dispersion of supported rhodium is inversely proportional to its content, the greatest decrease in the degree of dispersion being observed on silicon dioxide (Table 3). The activity of the catalyst reduced by hydrogen at an elevated temperature can be increased by a factor of approximately four by treating it with air at 50–200 °C.^{48, 50} This effect has been explained by the removal of hydrogen strongly bound to the surface, which reacts with difficulty.⁴⁸ On treating the rhodium catalyst with air, rhodium oxide is not formed.

With increase in the degree of dispersion of the supported rhodium, the per activity of the catalyst per unit mass of the latter increases, whilst the activity per unit surface of the metal remains approximately constant and close to that of rhodium black (Table 3).

Kinetic studies have shown^{42, 48} that in the presence of rhodium black the increase in the rate of reaction with increase in temperature in the range 15–28 °C at $P = 5$ MPa and $c = 0.4$ M corresponds to an apparent activation energy of 34 ± 2 kJ mol⁻¹. When the content of 3-thiolene 1,1-dioxide is between 0.07×10^{-3} and 0.8×10^{-3} M, the rate of reaction (20 °C, $P = 5$ MPa) on rhodium black and on 5% Rh/ Al_2O_3 is proportional to the concentration of the substrate. In the range of pressures P from 0.4 to 2 MPa (at 20 °C and $c = 0.4$ M), the rate of hydrogenation is proportional to the hydrogen pressure, whilst at a higher pressure ($P = 2$ – 7 MPa) it remains unchanged.

Nickel. The hydrogenation of 3-thiolene 1,1-dioxide in the presence of nickel catalysts has been investigated in fair detail. The patents published in the 1940s–1950s present numerous examples of hydrogenation on Raney nickel and nickel deposited on silicon dioxide.^{52–56}

In the absence of a solvent, the yield of thiolane 1,1-dioxide on Raney nickel was ~30% and the hydrogenation was accompanied by the marked decomposition of the substrate (65 °C, $P = 0.01$ MPa, $t = 20$ h).⁵⁴ In solutions in ethanol, water, and thiolane 1,1-dioxide at 20–30 °C and $P \leq 0.01$ MPa, the yield of the target product increased to 58%–100% with $W = 0.006$ – 0.29 mol h⁻¹,^{52, 53, 56} In the presence of an excess of

Table 3. The influence of the content of metallic rhodium in the supported catalyst on its specific surface, activity, and stability in the hydrogenation of 3-thiolene 1,1-dioxide (20 °C, $P = 5$ MPa, $c = 0.4$ M).^{42, 48}

Carrier	Content of Rh in catalysts/ $\mu\text{g m}^{-2}$	S_{sp} / $\text{m}^2 \text{g}^{-1}$ Rh	Activity		Stability	
			see ^a	see ^b	see ^c	see ^d
γ - Al_2O_3	30	280	250	175	—	—
	47	238	566	233	500	208
	125	217	916	208	833	175
	170	162	833	175	1250	250
	312	166	1670	200	1670	200
	570	139	3207	225	1670	200
SiO_2	78	86	242	142	—	—
	116	72	350	167	416	192
	195	57	500	175	670	233
AlSi	16	65	50	154	—	—
	31	—	100	—	160	—
	63	55	175	160	183	180
	115	—	250	—	—	—
	167	40	342	167	250	125
Activated charcoal	22	60	100	165	—	—
	41	60	200	167	170	140
	65	50	250	168	—	—
	102	40	330	170	250	125
Without carrier	170000	6	1850	306	1330	225

^a Expressed in mol h⁻¹ g⁻¹. ^b Expressed in mol h⁻¹ m⁻² Rh. ^c Expressed in mmol g⁻¹. ^d Expressed in mmol m⁻² Rh.

the catalyst, the 100% yield of thiolane 1,1-dioxide was attained already after 5 min (20 °C, $P \geq 30$ MPa, $c = 4.24$ M, $g_{\text{ct}} = 170$ g litre⁻¹), but for $g_{\text{ct}} = 5$ g litre⁻¹ it did not exceed 85% even after 7 h.⁵⁵ On the 72% Ni/ SiO_2 catalyst in thiolane 1,1-dioxide, exhaustive hydrogenation of 3-thiolene 1,1-dioxide in a flow system was attained at 27–30 °C, $P > 7$ MPa, and with the solution supplied at a space velocity of 3 h⁻¹.⁵⁴

Subsequently the study of this reaction in the presence of metallic nickel catalysts was continued. Unfortunately the results of different investigations do not always agree, possibly owing to the different degrees of purification of 3-thiolene 1,1-dioxide and the lack of monitoring of diffusional limitations.

According to the results of Virobyants and coworkers,^{44, 45} on Raney nickel at atmospheric pressure the hydrogenation of 3-thiolene 1,1-dioxide in solution in ethanol is slow and terminates only after 1.5–9.5 h (20 °C, $c = 0.19$ – 0.64 M, $g_{\text{ct}} = 0.7$ – 5 g litre⁻¹). An increase in pressure facilitates the hydrogenation and, for example, in methanol the rate of reaction reaches 0.23 mol h⁻¹ g⁻¹. The hydrogenation is slowest in thiolane 1,1-dioxide and water; in benzene, ethanol, and methanol, the reaction rates increase by factors of 2.5, 4, and 8 respectively (20 °C, $P = 6$ MPa, $c = 1.7$ M, $g_{\text{ct}} = 6$ g litre⁻¹). This agrees with other data,⁵⁷ according to which the rate of hydrogenation on Raney nickel in isopropyl alcohol is higher by a factor of 7–10 than in thiolane 1,1-dioxide (20 °C, $P = 4$ MPa). In the pressure range from 3 to 9 MPa, the rate of hydrogenation is proportional to P and at $P = 7$ – 14 MPa it changes little (20 °C, $c = 1.4$ M).⁴⁵ The slowness of the hydrogenation reaction of 3-thiolene 1,1-dioxide on Raney nickel even at an elevated hydrogen pressure has been confirmed by the results of Sapozhnikova *et al.*⁵⁸ An 87%–100% yield of thiolane 1,1-dioxide in isopropyl alcohol, thiolane 1,1-dioxide, or its mixture with water is attained after 6.5–8 h (30–40 °C, $P = 10$ MPa, $c = 1.4$ M). On the other hand, according to the results of Mashkina *et al.*⁴² in the kinetic region on Raney nickel ($S_{\text{sp}} = 70$ m² g⁻¹) thiolane 1,1-dioxide was formed with 100% yield after only 11 min and the rate of

reaction was $0.3 \text{ mol h}^{-1} \text{ g}^{-1}$ (20°C , $P = 5 \text{ MPa}$, $c = 0.4 \text{ M}$, $g_{\text{ct}} = 7.2 \text{ g litre}^{-1}$, $[\text{SO}_2] < 0.03 \times 10^{-3} \text{ M}$).

The modification of Raney nickel by adding metals increases its activity.⁵⁹ The catalytic properties are determined by the ratio Ni:Al in the alloy and by the method used to introduce additives. If the modification of nickel is carried out in the leaching stage by adding 0.1 mass %–1 mass % of copper, cobalt, chromium, or platinum, the activity of the catalyst increases by a factor of 1.1–1.6, whereas in the presence of 0.1 mass %–2 mass % of added vanadium and molybdenum the increase is by a factor of 1.5–3.0. The addition of molybdenum, vanadium, zirconium, or niobium to nickel in the fusion stage leads to the preparation of a catalyst the activity of which is higher by a factor of 3–6 than that of the unpromoted Raney nickel (Table 4). The surface of the nickel, determined from the degree of adsorption of thiophene, does not change as a result of the promotion.

Table 4. The influence of the promotion of Raney nickel on its catalytic properties in the hydrogenation of 3-thiolene 1,1-dioxide (20°C , $P = 5 \text{ MPa}$, $c = 0.25\text{--}0.38 \text{ M}$, $g_{\text{ct}} = 2.7\text{--}6.3 \text{ g litre}^{-1}$, $[\text{SO}_2] < 0.07 \times 10^{-3} \text{ M}$).⁵⁹

Promoting agent	Compound introduced into alkaline solution	Content of introduced promoting agent in catalyst (mass %)	Activity of catalyst ^a	Stability of catalyst ^b
Promotion of NiAl ₃ alloy in the leaching stage ^c				
None	—	—	17.5	250
Cu	Cu(NO ₃) ₂	0.1–1	19.4	250
Cr	Cr(NO ₃) ₃	1.0	27.7	290
Mo	(NH ₄) ₂ MoO ₄	0.1	6.7	275
Co	Co(NO ₃) ₂	0.1–1	22.3	217
V	NH ₄ VO ₃	1.0	51.6	583
Pt	H ₂ PtCl ₆	0.1–1	28.3	267
Promotion of the NiAl alloy in the leaching stage ^c				
None	—	—	11.7	50
V	V ₂ O ₅	0.25	16.7	100
V	NH ₄ VO ₃	0.6	34.2	125
Promotion in the fusion stage ^d				
None	—	—	4.5	33
Mo	—	1.0	13.3	200
Mo	—	7.5	21.7	183
Zr	—	1.0	18.3	130
Nb	—	1.0	28.7	233
V	—	4.7	13.3	83
V	—	14.8	16.7	117

^a Expressed in $\text{mol h}^{-1} \text{ g}^{-1}$. ^b Expressed in mmol g^{-1} . ^c Leaching conditions: 50°C , $[\text{KOH}] = 25 \text{ mass \%}$. ^d Leaching conditions: 100°C , $[\text{KOH}] = 15 \text{ mass \%}$ – $25 \text{ mass \%}$.

The Raney nickel catalyst obtained from a Ni–Al alloy doped with a series of metals exhibits an enhanced activity also in the hydrogenation reactions of other unsaturated compounds.⁶⁰ It has been postulated that doping with niobium and zirconium leads to an increase in the content of the intermetallic compound NiAl₃ in the alloy; molybdenum aluminides, which influence the degree of dispersion of nickel, are formed in the molybdenum-containing alloys.⁶¹ Doping of vanadium-containing alloys alters the energy of the bond between hydrogen and the surface and the rate of production of hydrogen.⁶²

Nickel on a carrier is also used as a catalyst of the hydrogenation of 3-thiolene 1,1-dioxide. In the presence of 50 mass % of nickel on chromium trioxide or silicon dioxide, the initial rate of reaction (1 min after its onset) in isopropyl alcohol at atmospheric pressure is $0.10\text{--}0.15 \text{ mol h}^{-1} \text{ g}^{-1}$, but exhaustive hydrogenation

is attained only after 1 h and the average rate of reaction over this period is only $0.017 \text{ mol h}^{-1} \text{ g}^{-1}$ ($20\text{--}30^\circ \text{C}$, $c = 0.42 \text{ M}$, $g_{\text{ct}} = 20 \text{ g litre}^{-1}$).^{46, 63–66} The addition of platinum to the nickel–chromium catalyst does not alter its activity.^{67, 68} An increase in pressure promotes an increase in the rate of hydrogenation of 3-thiolene 1,1-dioxide, which is $0.19\text{--}0.33 \text{ mol h}^{-1} \text{ g}^{-1}$ at $P = 2\text{--}5 \text{ MPa}$ ($20\text{--}35^\circ \text{C}$, $c = 0.4\text{--}1 \text{ M}$).^{64, 65}

The kinetics of the hydrogenation of 3-thiolene 1,1-dioxide on Raney nickel and on the nickel–chromium catalyst are approximately the same.^{46, 47, 57, 63–65, 69–72} In the hydrogenation of pure 3-thiolene 1,1-dioxide ($[\text{SO}_2] < 0.03 \times 10^{-3} \text{ M}$), the reaction takes place in the kinetic region, provided that the catalyst grain size does not exceed 0.1 mm. The reaction order depends on the substrate concentration and hydrogen pressure ranges.

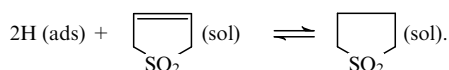
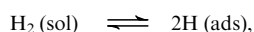
At atmospheric pressure, the reaction is of zero order with respect to 3-thiolene 1,1-dioxide dissolved in isopropyl alcohol or thiolane 1,1-dioxide in the concentration ranges $c = 0.5\text{--}5 \text{ M}$ (35°C , Ni/Cr₂O₃) and $c = 0.1\text{--}0.8 \text{ M}$ (20°C , Raney nickel).^{63, 70} On the other hand, when the reaction was carried out in another study⁴⁷ on Raney nickel in ethanol, it was found to be of first order with respect to 3-thiolene 1,1-dioxide ($c \leq 0.07 \text{ M}$, $15\text{--}45^\circ \text{C}$). At an elevated pressure, the reaction order with respect to 3-thiolene 1,1-dioxide changes from zero in the range $c = 1.5\text{--}5.3 \text{ M}$ (30°C , $P = 0.7\text{--}4 \text{ MPa}$) to first in the range $c = 0.1\text{--}2.5 \text{ M}$ ($30\text{--}35^\circ \text{C}$, $P = 0.7\text{--}4 \text{ MPa}$). The reaction order with respect to hydrogen also changes from first in the pressure range $0.01\text{--}2.5 \text{ MPa}$ ($20\text{--}35^\circ \text{C}$, $c = 0.53\text{--}3 \text{ M}$) to zero at $P = 0.7\text{--}4 \text{ MPa}$ ($30\text{--}35^\circ \text{C}$, $c = 0.53\text{--}3 \text{ M}$).^{57, 63, 64, 70}

The dependence of the reaction order on Raney nickel on the reaction conditions has been explained by the change in the mechanism of the hydrogenation of 3-thiolene 1,1-dioxide.⁵⁷ At $P \leq 0.1 \text{ MPa}$ (zero order with respect to the substrate and first order with respect to hydrogen), 3-thiolene 1,1-dioxide is hydrogenated under conditions where its concentration in solution greatly exceeds the concentration of hydrogen owing to the low solubility of the latter. The ratio of the reactant concentrations on the catalyst surface during the reaction at $P = 0.1 \text{ MPa}$ may be inferred from the change in the catalyst potential. The reversible hydrogen potential of Raney nickel is $540\text{--}610 \text{ mV}$ (30°C). When 3-thiolene 1,1-dioxide is introduced into the solution, the potential shifts to the anodic region by a $300\text{--}400 \text{ mV}$,^{47, 57, 65} which indicates the preferential adsorption of the substrate and the displacement of a large proportion of hydrogen from the surface by the latter. The 3-thiolene 1,1-dioxide substrate is rapidly adsorbed on nickel and the limiting degree of its adsorption from solutions is $\sim 0.2 \text{ g per gram of nickel}$. Under these conditions, the degree of surface coverage of nickel by 3-thiolene 1,1-dioxide is high and the rate of hydrogenation is therefore independent of the substrate concentration. The rate of the process is limited by the activation of hydrogen.⁵⁷ Sokol'skaya and Reshetnikov,⁴⁷ who investigated the hydrogenation of 3-thiolene 1,1-dioxide in ethanol on Raney nickel ($15\text{--}45^\circ \text{C}$, $P = 0.1 \text{ MPa}$, $c < 0.1 \text{ M}$), arrived at the same conclusion. At pressures above atmospheric, the concentration of hydrogen in solution and on the nickel surface increases and the reactant ratio on the surface changes, which affects the reaction mechanism.

In order to account for the observed kinetics in the absence of diffusional complications, one employs the kinetic schemes for liquid-phase hydrogenation reactions on inhomogeneous surfaces and the corresponding specific kinetic equations.⁷³ It has been suggested that there is equilibrium between the concentrations of the reactants on the surfaces and in the liquid phase. The lack of dependence of the rate of hydrogenation of 3-thiolene 1,1-dioxide on the weight of the catalyst sample permitted the conclusion that the rate of the process is not limited by the dissolution of hydrogen and that one may use instead of the hydrogen concentration in solution the hydrogen pressure, which is proportional to it.

The first order of the reaction with respect to the substrate at a constant hydrogen pressure, the high rate of adsorption of

3-thiolene 1,1-dioxide, and the occurrence of the reaction at high surface coverages by the substance hydrogenated⁵⁷ provide grounds for the hypothesis that at $c \leq 1.6$ M the reaction takes place in accordance with the Scheme 4.



Scheme 4

If the rate of reaction is limited by the interaction of the dissolved 3-thiolene 1,1-dioxide with the adsorbed hydrogen and the reaction proceeds at high surface coverages by hydrogen, its rate is described by the equation

$$W = kc_1.$$

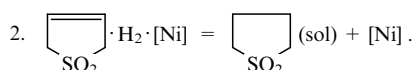
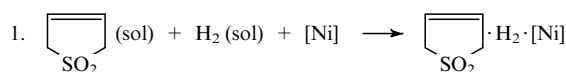
Here c_1 is the concentration of 3-thiolene 1,1-dioxide and

$$k = \frac{(\vec{k}_2)_0}{m'},$$

where $(\vec{k}_2)_0$ is the rate constant for the second stage in the forward direction and m' is a constant characterising the degree of inhomogeneity of the catalyst surface.

The overall zero order of the reaction with respect to both reactants, observed under the conditions of hydrogenation of Raney nickel at a high 3-thiolene 1,1-dioxide concentration in solution and an elevated hydrogen pressure, has been explained⁴⁷ by the occurrence of the reaction *via* a stage involving the formation of a complex incorporating hydrogen, 3-thiolene 1,1-dioxide, and nickel (Scheme 5).

Scheme 5



If the process is limited by the consumption of the complex (stage 2) and proceeds at a high surface coverage by both reactants, its rate is described by the equation

$$W = k,$$

$$\text{where } k = \frac{(\vec{k}_2)_0}{m'}.$$

In a flow system on large 50% Ni/Cr₂O₃ catalyst grains, the rate of hydrogenation of 3-thiolene 1,1-dioxide is lower than in a static system on fine grains.^{64, 69, 71, 72, 75} The rate of hydrogenation increases with decrease in the catalyst grain size and with increase in the linear rate of supply of the starting material. The activation energy is only 8.4 kJ mol⁻¹. These results indicate that the reaction proceeds in the external diffusion region. At $c = 1.06$ – 2.65 M and $P < 0.6$ MPa, the rate of hydrogenation is proportional to the hydrogen pressure and is independent of the concentration of 3-thiolene 1,1-dioxide. Under these conditions, the process is limited by the rate of supply of hydrogen to the outer surface of the catalyst (external diffusion region with respect to hydrogen). At pressures exceeding 0.6 MPa, the rate of supply of hydrogen to the surface increases and the rate of reaction ceases to depend on the hydrogen pressure (zero order with respect to hydrogen) but becomes proportional to the concentration of 3-thiolene 1,1-dioxide. The slowest stage determining the rate of hydrogenation becomes the rate of arrival of the substrate on the outer surface of the catalyst, *i.e.* the process passes to the external diffusion region with respect to 3-thiolene 1,1-dioxide.

In the kinetic region, the rate of reaction in a flow reactor is expressed by the equation

$$W = kHXP,$$

where k is the reaction rate constant, H the solubility coefficient of hydrogen, the X concentration of hydrogen, and P the pressure.

On the other hand, if the rate of mass transfer is less than the rate of reaction and the process proceeds either at low hydrogen concentrations or low 3-thiolene 1,1-dioxide concentrations, then the equations for the rate of reaction assume the following forms respectively:

$$W = aHk_1P \quad \text{and} \quad W = k_2X,$$

where a is the stoichiometric coefficient and k_1 and k_2 are the mass transfer coefficients of hydrogen and 3-thiolene 1,1-dioxide respectively in the direction of the diffusion flux. These equations describe satisfactorily the experimental data on the hydrogenation of 3-thiolene 1,1-dioxide to thiolane 1,1-dioxide in a flow reactor.

Since under the conditions where the reaction takes place in the external diffusion region with respect to hydrogen the flow reactor becomes similar to the packed column employed for the adsorption of gases, the equations for mass transfer in a film adsorber may be employed for the calculations if it is assumed that the catalyst assumes the role of the packing and the column operates in the film regime.^{69, 71} The principal technological parameters of the process have been selected and a scheme for the synthesis of thiolane 1,1-dioxide has been recommended on the basis of a detailed study of the kinetics of the hydrogenation of 3-thiolene 1,1-dioxide on the nickel-chromium catalyst.^{64, 69, 75}

Palladium. In the early studies (see the present author's previous review¹), it was already noted that, in the presence of metallic palladium catalysts, the multiple bond of 3-thiolene 1,1-dioxide is fully saturated and thiolane 1,1-dioxide is formed in 100% yield. At atmospheric pressure in aqueous solution on colloidal palladium, the reaction is slow with the rate $W = 0.004$ mol h⁻¹ g⁻¹ (20 °C, $c = 0.2$ M, $g_{\text{ct}} = 250$ g litre⁻¹).⁴ When palladium is deposited on charcoal, the rate of reaction in ethanol increases to 0.017–0.05 mol h⁻¹ g⁻¹ (20 °C, $c = 0.35$ – 1.0 M).^{44, 76} In the presence of 5% Pd/BaSO₄ in ethanol, exhaustive hydrogenation takes place over a period of 3–4 min (30 °C, $P = 0.1$ MPa, $c = 0.077$ M, $g_{\text{ct}} = 1.72$ g litre⁻¹) at the rate $W = 0.92$ mol h⁻¹ g⁻¹.⁴⁷

At an elevated pressure, the rate of hydrogenation of purified 3-thiolene to which 1,1-dioxide in the kinetic region in isopropyl alcohol 10 mass % of thiolane 1,1-dioxide has been added increases appreciably. Thus on palladium black the 100% yield of thiolane 1,1-dioxide is attained after less than 1 min and $W = 13.7$ mol h⁻¹ g⁻¹ {20 °C, $P = 5$ MPa, $c = 0.37$ M [SO₂] = 0.028×10^{-3} M}.⁴² Under these conditions, the reaction rates are 4.2, 4.0, 3.4, and 1.3 mol h⁻¹ g⁻¹ on catalysts containing 2 mass % of Pd on γ -Al₂O₃, AlSi, SiO₂, and activated charcoal respectively.⁷⁷

The rate of hydrogenation of 3-thiolene 1,1-dioxide is influenced by the nature of the solvent. On the 5% Pd/Al₂O₃ (20 °C, $P = 5$ MPa, $c = 0.4$ M) in isopropyl alcohol, the reaction was very rapid, in 1-butanol the rate of hydrogenation fell by a factor of 1.2, and in *tert*-butyl alcohol and thiolane 1,1-dioxide it fell by a factor of 10.⁷⁸ In a mixture of isopropyl alcohol and 5 mass %–20 mass % of thiolane 1,1-dioxide, the rate of reaction was the same as in pure isopropyl alcohol. The addition of 2 mass %–10 mass % of water to isopropyl alcohol reduces the rate of hydrogenation by a factor of 1.2–2.5. In isopropyl alcohol, the rate of reaction is a maximum in a neutral medium, the rate diminishing approximately by a factor of 2 when potassium hydroxide or hydrochloric acid is added to the solution at a concentration of 2.5×10^{-3} M.⁷⁸

The kinetics of the hydrogenation of 3-thiolene 1,1-dioxide in pure isopropyl alcohol or isopropyl alcohol to which 10 mass % of thiolane 1,1-dioxide had been added were investigated on palladium-containing catalysts of different compositions.^{42, 78, 79}

On palladium black and on the 2.5% Pd/Al₂O₃ catalyst, the reaction takes place in the kinetic region where the grain size is 0.06–0.1 mm (20 °C, $P = 5$ MPa, $c = 0.4$ M). On catalysts of

different composition in the range of pressures P from 0.1 to 1.0 MPa, the rate of hydrogenation at 20 °C and $c = 1.4$ M is proportional to the hydrogen pressure, but at pressures in the range 1–6 MPa it remains constant. At $P = 5$ MPa, the rate of hydrogenation is proportional to the concentration of 3-thiolene 1,1-dioxide (at $c = 0.1$ –1 M), but at $P = 0.1$ MPa it remains unchanged in the range of concentrations c from 0.04 to 0.21 M.^{42, 78, 79} However, it has been found⁴⁷ that the rate of hydrogenation of 3-thiolene 1,1-dioxide on the 5% Pd/BaSO₄ catalyst in ethanol is proportional to the substrate concentration (at $c < 0.077$ M); the activation energy for the reaction was 19 kJ mol⁻¹ (15–45 °C, $P = 0.1$ MPa).

The mechanism of the hydrogenation of 3-thiolene 1,1-dioxide on palladium-containing catalysts is apparently the same as on nickel catalysts.^{47, 48} The necessary stages of the formation of thiolane 1,1-dioxide are the adsorption of the reactants and their activation on the catalyst surface.

The adsorption of 3-thiolene 1,1-dioxide on palladium at 20 °C and $P = 0.1$ MPa is very rapid and its rate cannot therefore be determined. The ratio of the surface concentrations of the reactants during the reaction was estimated by measuring the catalyst potential at atmospheric pressure in alcoholic solutions.^{47, 67}

The reversible hydrogen potential of the palladium catalyst is 630–640 mV. After the introduction of 3-thiolene 1,1-dioxide into a neutral solution, the potential shifted to the anodic region by 100–120 mV (5% Pd/BaSO₄, 30 °C, $c = 0.077$ M, solution in ethanol)⁴⁷ or by 130 mV (2% Pd/C, 20 °C, $c = 0.25$ M, solution in isopropyl alcohol).⁶⁷ According to the existing ideas,⁴⁷ such a potential shift indicates a relatively weak bond between hydrogen and the catalyst and the displacement of hydrogen from the surface by the adsorbed 3-thiolene 1,1-dioxide and also a high surface coverage by the dioxide.

In principle, it is possible that at $P > 2$ MPa the reaction proceeds *via* an impact mechanism, *i.e.* *via* the interaction of molecular hydrogen with the adsorbed 3-thiolene 1,1-dioxide. However, in this case the rate of hydrogenation should have depended on the hydrogen pressure. Since this conflicts with experimental results, it was concluded⁴⁷ that the hydrogen adsorbed on the palladium surface participates in the reaction.

Hydrogen, which can be adsorbed on palladium at a high rate,³⁹ can participate in the hydrogenation. Thus, on hydrogen-saturated palladium black (20 °C, $P = 0.1$ MPa, $t = 30$ min) in nitrogen, 3-thiolene 1,1-dioxide is hydrogenated at a rate of 14 ml H₂ min⁻¹ g⁻¹. However, this is an order of magnitude less than the rate of hydrogenation in a H₂ atmosphere, *i.e.* the hydrogen dissolved in palladium hydrogenates only part of the substrate and a continuous resupply of the surface by hydrogen is required. The strength of the bond between hydrogen and the catalyst should then lie within definite limits.^{39, 78} This has been confirmed by the results of experiments on hydrogenation on palladium-containing catalysts in which the bond between hydrogen and palladium was changed by means of modifying additives.⁸⁰ Thus, on a hydrogen-saturated 1.5% Pd + 0.5% Pt/C specimen, the anodic potential shift on hydrogenation of 3-thiolene 1,1-dioxide is 90 mV, *i.e.* smaller by 40 mV than on an unpromoted 2% Pd/C specimen.⁶⁷ This indicates a strengthening of the bond between hydrogen and the surface. The rate of hydrogenation of 3-thiolene 1,1-dioxide in isopropyl alcohol on the promoted catalyst decreases from 0.032 to 0.018 mol h⁻¹ g⁻¹ (20 °C, $P = 0.1$ MPa, $c = 0.254$ M). The introduction of alkali into the hydrogenated solution leads to the formation of an unduly strong bond between hydrogen and the palladium surface³⁹ and the activity of the catalyst diminishes. Thus, on the 4% Pd/Al₂O₃ catalyst the rate of hydrogenation of 3-thiolene 1,1-dioxide in a neutral solution is higher by a factor of 3 than after the addition of sodium hydroxide at a concentration of 2.25×10^{-3} M (20 °C, $P = 5$ MPa, $c = 0.4$ M).²²

Under the conditions of the reduction of the catalyst at an elevated temperature (300 °C), a strong hydrogen–palladium

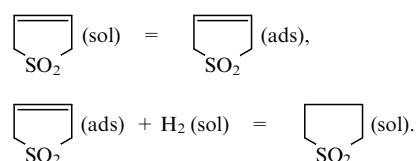
bond is formed and such hydrogen is insufficiently reactive and is desorbed with difficulty.⁸¹ Its removal from the surface *in vacuo* (10⁻³ mm Hg at 300 °C, $t = 20$ h) or on treatment with air (50–250 °C, $t = 2$ h) increases the activity of the catalyst in the hydrogenation of 3-thiolene 1,1-dioxide by a factor of 2.⁸² On comparing the specific surfaces of palladium found from the chemisorption of oxygen and by the method involving the poisoning of the catalyst during hydrogenation, one may conclude that the increase in activity is due to the increase in the number of active sites on the surface after the removal of hydrogen by oxidative treatment.

On palladium black and supported catalysts (2 mass %–10 mass % Pd/γ-Al₂O₃) the reaction orders with respect to hydrogen and 3-thiolene 1,1-dioxide in isopropyl alcohol with added 10% of thiolane 1,1-dioxide depend on the hydrogenation conditions (see above).

The activity of palladium decreases after the introduction into the hydrogenated solution of very small amounts of sulfur dioxide and hydrogen sulfide. The exponential decrease in the activity of the catalyst with increase in the concentration of the poison in solution observed under these conditions is associated with the energy inhomogeneity effect in the real adsorbed layer.

The kinetics observed on palladium catalysts have been examined in a generalised form.⁷⁸ At low pressures ($P = 0.1$ –1 MPa), the concentration of 3-thiolene 1,1-dioxide in solution appreciably exceeds the concentration of hydrogen because of the low solubility of the latter. Under the reaction conditions, the substrate displaces hydrogen from the surface and the latter proves to be saturated by 3-thiolene 1,1-dioxide. It is most likely that the reaction proceeds in accordance with the Scheme 6.

Scheme 6



The zero order of the reaction with respect to 3-thiolene 1,1-dioxide and the first order with respect to hydrogen can be accounted for by the limitation of the process by the stage involving the interaction of the adsorbed substrate with hydrogen. The kinetic equation assumes the following form in this instance:

$$W = k,$$

$$\text{where } k = \frac{(\vec{k}_2)_0 c_2}{m'}.$$

At a hydrogen pressure in excess of 2 MPa, the process kinetics change owing to the alteration of the reaction mechanism. It has been suggested⁷⁸ that an increase in pressure promotes an increase in the concentration of hydrogen in solution and facilitates its access to the catalyst surface. This induces an increase in the degree of surface coverage by hydrogen, which becomes comparable to the degree of surface coverage by the substrate. In this case, the process is described by the kinetic equation which follows from Scheme 4.

The activity of palladium-containing catalysts in the hydrogenation reaction of 3-thiolene 1,1-dioxide depends significantly on the area of the accessible palladium surface. Massive palladium, obtained by the reduction of an aqueous solution of palladium chloride by formalin in an alkaline medium, is characterised by $S_{sp} = 5$ m² g⁻¹, while the specimen prepared by oxidising palladium chloride with sodium nitrate and subsequent reduction with hydrogen is characterised by $S_{sp} = 22$ m² g⁻¹. The activities of these catalysts per gram of palladium (20 °C, $P = 5$ MPa, $c = 0.4$ M) are significantly different (466 and 1850 mol h⁻¹ g⁻¹ respectively), but their activities per unit surface are similar (93 and 84 mol h⁻¹ m⁻² Pd respectively).⁴²

It has been established that the degree of dispersion of palladium on carriers exerts a strong influence on the activity of hydrogenation catalysts.^{77, 79, 83} The degree of dispersion of palladium was measured by several independent methods: by X-ray phase analysis (XPA), by electron microscopy (EM), from the chemisorption of oxygen, carbon monoxide, and sulfur dioxide, and by the method involving the poisoning of the catalyst by a sulfur poison in the course of hydrogenation. All the methods yielded similar degrees of dispersion of palladium. It follows from the data obtained that most of the palladium is in the crystalline state. The degree of dispersion of palladium depends on its content in the catalyst, the nature of the carrier, its specific surface, the method of preparation of the specimen, and the presence of certain additives.

Palladium deposited on alumina, aluminosilicate, and activated charcoal has a high degree of dispersion, whilst palladium deposited on a zeolite, corundum, and carborundum has a low degree of dispersion (Tables 5 and 6).^{77, 79, 83, 84}

Table 6 shows that the degree of dispersion of palladium increases linearly with decrease in its surface concentration. The smallest change in the degree dispersion as a function of the metal concentration on the surface is observed when palladium is deposited on activated charcoal and the greatest change is observed when it is deposited on silicon dioxide. This difference can be explained by the different strengths of the Pd-carrier bond and the associated difference between the surface mobilities of palladium. However, on the whole the overall surface area of the metal increases up to a certain limiting content of the metal on the

carrier and the rate of hydrogenation of 3-thiolene 1,1-dioxide calculated per unit mass of the catalyst therefore increases.

For a constant content of palladium, the degree of its dispersion may be regulated not only by varying the nature of the carrier but also by varying the composition of the impregnating solution and by subjecting the specimen to an additional chemical treatment before reduction. We shall consider this in relation to the Pd/Al₂O₃ catalyst prepared by impregnating the carrier with an aqueous solution of a palladium compound with subsequent reduction by hydrogen at 300 °C for 30 h.^{84–88} The degree of dispersion of palladium in specimens obtained by employing a palladium chloride solution in hydrochloric acid proved to be various (Table 6). In the presence of an excess of hydrochloric acid (HCl: PdCl₂ = 2:1), the Pd²⁺ complex contains only chloride ligands, is weakly bound to the γ-Al₂O₃ surface, and is relatively mobile. Its heat treatment therefore results in the formation of comparatively large palladium agglomerates (specimen No. 1 in Table 6). For the ratio HCl: PdCl₂ = 1:1 (specimen No. 2), the composition of the palladium ion complex includes also OH groups, which promotes stronger binding of palladium to the γ-Al₂O₃ surface and hence a decrease in the degree of crystallisation of the metal. However, unduly strong binding of the Pd²⁺ ion to the carrier, as happens for example when the Pd(NH₃)₄Cl₂ complex is employed (specimen No. 3), makes it necessary to increase the reduction temperature to 400 °C and this tends to intensify crystallisation and promotes a sharp decrease in the degree of dispersion of palladium. Aluminium oxide impregnated with a hydrochloric acid solution of PdCl₂ and subjected to an additional treatment with potassium

Table 5. Dependence of the specific surface of palladium, its activity, and its stability on the composition of the catalyst (20 °C, $P = 5$ MPa, $c = 0.4$ M).^{77, 83}

Carrier	S_{BET} /m ² g ⁻¹	Surface concentration of Pd /μg m ⁻²	S_{sp} /m ² g ⁻¹ Pd	Activity		Stability	
				mol h ⁻¹ g ⁻¹	mol g ⁻¹ m ⁻² Pd	mmol g ⁻¹	mmol m ⁻² Pd
γ-Al ₂ O ₃	200	25	280	83	62	—	—
	200	50	220	185	87	250	113
	200	100	195	292	75	417	107
	200	150	160	416	88	500	104
	200	250	140	580	83	670	95
	200	400	125	830	85	—	—
	200	500	130	1000	67	1330	103
	200	750	100	1460	96	—	—
	200	1000	80	1450	92	—	—
	242	83	210	330	79	417	100
	119	170	110	217	98	242	110
	81	247	80	133	83	158	99
SiO ₂	300	17	100	25	50	—	—
	300	33	80	45	58	67	83
	300	67	60	67	56	—	—
	300	100	45	85	60	125	88
	300	167	30	127	83	—	—
	300	267	30	167	70	—	—
AlSi	360	14	314	100	63	—	—
	360	27	280	133	50	250	92
	360	56	200	200	50	—	—
	360	83	130	250	64	330	83
Activated charcoal	510	20	195	108	54	250	67
	510	40	165	210	63	—	—
	510	60	210	290	45	500	83
	510	100	170	351	42	—	—
NaX	—	30	—	50	—	—	—
CaX	—	30	—	56	—	—	—
NaY	—	28	—	43	—	—	—

Table 6. The influence of the method of preparation of the 5% Pd/Al₂O₃ catalyst on the degree of dispersion of palladium, its activity, and its stability in the hydrogenation of 3-thiolene 1,1-dioxide.^{84, 85}

No. of Specimen	S_{sp} /m ² g ⁻¹ Pd	Pd particle size /nm			Activity		Stability	
		chemisorption of O ₂	XPA	EM	mol h ⁻¹ g ⁻¹	mol h ⁻¹ m ⁻² Pd	mmol g ⁻¹	mmol m ⁻² Pd
1	100	6.0	10.0	11	500	100	500	100
2	140	3.5	8.0	10	580	83	660	96
3	20	20.0	24.0	25	60	58	—	—
4	180	2.5	(see ^a)	—	750	88	1170	117
5	180	2.3	(see ^a)	—	833	87	—	—
6	210	2.0	(see ^a)	—	100	100	1160	118
7	180	2.3	(see ^a)	—	830	92	100	108

^a X-Ray-amorphous specimen.

hydroxide, sodium carbonate, or hydrogen sulfide before reduction with hydrogen (specimens Nos 4–6) or the same specimen impregnated with palladium nitrate (No. 7) contain a water-insoluble palladium oxide or sulfide, which reduces the mobility of the metal on the surface during reduction and promotes an increase in its degree of dispersion.

With increase in the specific surface of palladium, its activity in the hydrogenation of 3-thiolene 1,1-dioxide per unit mass of the specimen also increases, *i.e.* from the standpoint of increasing the productivity of the catalyst it is convenient to employ specimens with a higher palladium content on the carrier. However, the activity per m² of the palladium surface when the size of the crystallites is up to 20 Å remains approximately constant (within the limits of 20 rel. %) and hardly differs from the specific activity of palladium black (Tables 5 and 6). Thus in this case too Borekov's rule holds.⁷⁴ According to this rule, the specific catalytic activities of catalysts having the same composition are approximately constant.

In many instances, the degree of dispersion of palladium increases when other elements are added to it.^{67, 89, 93} The addition of 3 mass % of boron to palladium black or the 5% Pd/Al₂O₃ catalyst increases the specific surface of palladium and the activity of the catalyst per unit mass of the latter increases by a factor of 1.5–2.^{89, 93} In order to increase the activity of palladium (both massive and deposited on γ -Al₂O₃), it has been suggested that other Group VIII metals be added to the catalyst.^{67, 90, 93} The activity depends on the concentration of the additive introduced and passes through a maximum at a definite content of the latter (Table 7). The passage of the catalytic activities of mixed palladium-containing catalysts through a maximum as a function of composition has been observed also in the hydrogenation of other unsaturated compounds. This phenomenon has been unambiguously explained.³⁹ It has been postulated that the additives alter the amount and form of the sorbed hydrogen and also the energy of its bond with the surface. However, it is difficult to test this experimentally. It may be that the alloy should have a definite electronic structure and that an activity maximum is attained when the number of vacancies in the *d* layer per metal atom is unity.³⁹ However, contrary to experimental data, a catalytic activity maximum should not be observed in this case on Pd–Pt alloys, since both metals have the same number of vacancies (0.6). The additives can influence the electronic configuration of palladium or can alter the degree of its dispersion.^{91, 92}

It is difficult to determine the surface areas of two different supported metals separately. Therefore, in order to justify the important role of the degree of dispersion of palladium, indirect evidence, obtained in a study of mixed oxides without a carrier which are solid solutions according to XPA data, was resorted to.^{67, 93} It was found that the activity of palladium oxide ($S_{sp} = 25$ m² g⁻¹) in the hydrogenation of 3-thiolene 1,1-dioxide is very high and amounts to 1700 mol h⁻¹ g⁻¹, so that complete reduction is attained after 1 min (20 °C, *P* = 5 MPa, *c* = 0.38 M,

$g_{ct} = 0.54$ g litre⁻¹). The palladium oxide is then fully reduced to the metal. Ruthenium and iridium oxides ($S_{sp} = 114$ and 162 m² g⁻¹ respectively) are appreciably less active under the conditions indicated (54 and 2.5 mol h⁻¹ g⁻¹ respectively), while rhodium oxide ($S_{sp} = 160$ m² g⁻¹) is completely inactive. Ruthenium and iridium oxides are reduced much more slowly in alcohol

Table 7. The influence of the modification of palladium catalysts on their activity and stability in the hydrogenation of 3-thiolene 1,1-dioxide (20 °C, *P* = 5 MPa, *c* = 0.38 M).^{67, 89, 93}

Modifying agent	Content in catalyst (mass %)		S_{sp} /m ² g ⁻¹	Activity ^a	Stability /mmol g ⁻
	Pd	modifying agent			
Pd/ γ -Al ₂ O ₃					
None	5.0	0	140 ^b	583	667
B	4.85	0.15	200 ^b	830	1000
Mn	4.75	0.25	—	900	1250
	4.5	0.5	—	900	1125
Ru	4.5	0.5	—	1024	1000
Rh	4.5	0.5	—	1170	1165
Ir	4.75	0.25	—	1083	830
Pt	4.25	0.75	—	1025	917
Pd without carrier					
None	100	0	5	575	1330
Ru	90	10	17	1450	1830
	75	25	58	2810	2500
	50	50	78	1930	—
	20	80	130	762	—
	0	100	114	54	250
	95	5	18	2540	—
Pt	85	15	24	3920	1670
	50	50	37	4600	—
	25	75	81	4230	1665
	0	100	88	2300	—
	90	10	45	3024	2917
	75	25	74	3215	5000
Rh	50	50	104	5048	6670
	30	70	103	1400	1670
	20	80	96	174	—
	0	100	162	0	—
	95	5	37	3465	1667
	90	10	43	3265	1670
Ir	75	25	51	408	—
	0	100	162	8	—

^a Expressed in mol h⁻¹ g⁻¹. ^b The specific surface of palladium. In the remaining cases, the specific surface of the catalyst determined by the BET method is given.

at 20 °C than palladium oxide. The complete reduction of Rh_2O_3 by hydrogen to metallic rhodium does not occur until 300 °C over a period of 2 h. Under the conditions of brief (0.5–1 min) saturation of the catalyst with hydrogen before the experiment and when 3-thiolene 1,1-dioxide is hydrogenated during the same period, only palladium oxide is reduced but not the oxides of other metals. The overall surface area of palladium and other platinum group metals in the mixed catalyst is greater than the surface area of unpromoted palladium. One may therefore assume that the increase in the activity of the catalyst in the presence of additives is associated with the increase in the degree of dispersion of palladium. A similar conclusion was reached also in the study of other palladium-containing bimetallic systems. When ruthenium is introduced into PdC or when lanthanum is introduced into Pd/SiO₂, the degree of dispersion of palladium increases.

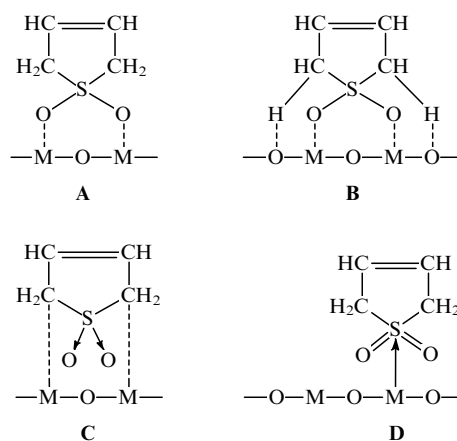
V. The resistance of metallic catalysts to sulfur

For metallic catalysts used in the low-temperature hydrogenation of various unsaturated substances, sulfur compounds are frequently catalytic poisons. The metal is deactivated as a result of the competitive chemisorption of the poison on the active centres (see the relevant reviews^{94–97}).

Sulfur compounds are strongly chemisorbed on the metal, forming a donor-acceptor bond with the latter.⁹⁴ Compounds of bivalent and tetravalent sulfur, having lone electron pairs, can participate in this process. However, sulfur-containing molecules lose their toxicity when all the valence orbitals of sulfur are saturated as a result of the formation of strong bonds with other elements, as happens, for example, in hexavalent sulfur compounds. The decrease in activity may be caused also by the change in the composition of the catalytically active component. Thus the interaction of hydrogen sulfide or certain organic sulfur compounds with the metal may entail the formation of the metal sulfide, which only weakly activates hydrogen and therefore exhibits a low activity in low-temperature hydrogenation processes.¹⁵

The chemical properties of sulfones have been considered in a number of studies.^{6,40,98} The sulfur atom of the sulfone has no lone pairs and therefore has no electron-donating capacity. The bond between sulfur and oxygen is mainly semipolar ($\text{O} \leftarrow \text{S} \rightleftharpoons$) but it also has partial double bond character (the $p_\pi-d_\pi$ $\text{O}=\text{S}$ bond). It is formed as a result of the interaction of the lone pair of oxygen with the unoccupied d orbital of the sulfur atom. The presence of a large positive charge on the sulfur atom increases the capacity of sulfones for $p-d$ conjugation and this tends to increase the acidity of the α -hydrogen atom of the sulfone. The oxygen atom in the sulfone has excess negative charge and this permits the formation of adducts *via* the oxygen atom. Thus metal compounds in solution form a donor-acceptor bond with charge transfer from the oxygen atom of sulfonyl group to the metal atom.^{14,98}

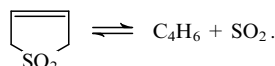
Knowing the properties of sulfones, one may put forward a hypothesis concerning the probable surface forms of 3-thiolene 1,1-dioxide formed when it comes into contact with the metal and the carrier. Apart from the π -olefin complex, the formation of which activates the multiple bond and leads to its reduction with formation of thiolane 1,1-dioxide (see Scheme 3), other surface structures can also arise (Scheme 7). The formation of bonds between the metal and the oxygen atoms of the sulfonyl group (**A**) is most probable. There is also a possibility of the coordination of the α -hydrogen atoms of the sulfone to the oxygen atoms of the carrier (**B**) and of the α -carbon atoms to the metal atoms (**C**) as well as the formation of a complex as a result of the interaction of the electrons of the metal atom with the d orbital of sulfur



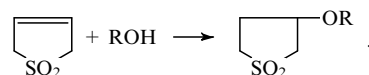
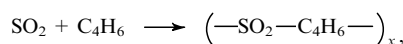
Scheme 7

(a $d_\pi-d_\pi$ bond) (**D**). The formation of a complex on the catalyst surface may entail the weakening and dissociation of the C–S bonds in the 3-thiolene 1,1-dioxide molecule.¹⁴

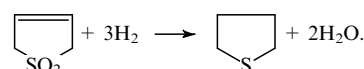
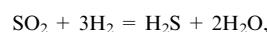
On dissociation of both C–S bonds in 3-thiolene 1,1-dioxide, buta-1,3-diene and sulfur dioxides are formed.



This reaction occurs even at room temperature and is accelerated as the temperature is raised. Above 100 °C, vigorous decomposition of 3-thiolene 1,1-dioxide begins. Since the hydrogenation of 3-thiolene 1,1-dioxide is an exothermic reaction (with a heat of 113 kJ mol^{–1}), inadequate removal of the heat evolved may promote the decomposition of the substrate. The primary products of the decomposition of 3-thiolene 1,1-dioxide under hydrogenation conditions react with formation of polysulfones and 3-alkoxythiolane 1,1-dioxides.



Divalent sulfur compounds, which are poisons for metallic catalysts may also be formed.



When the degree of poisoning of catalysts is estimated, it is very important to select correctly the criteria of resistance to sulfur. There is no unanimous view concerning this question. In order to compare catalysts, the reactions of the sulfur-containing raw material are frequently carried out under standard conditions (at a definite temperature, pressure, contact time, and concentration of the poison)¹⁰⁰ and the resistance of the catalyst to sulfur is inferred from the yield of the product or from the degree of conversion of the substrate after a specific time interval. Such a measure of resistance to sulfur cannot be regarded as correct, its unsuitability being particularly evident when catalysts with different surface areas are compared.

Since the reaction rate referred to unit surface of the active component, measured in the kinetic region, is the generally accepted characteristic of catalytic activity, in determining the resistance of catalysts to sulfur it is useful to estimate the change in specific activity under the influence of poisons. In order to determine the resistance to sulfur, in the general case it is sufficient to determine the amount of poison in the reaction mixture for

which the specific activity falls to a specified value. The main cause of the deactivation of the catalyst is frequently the decrease in the number of accessible active centres as a consequence of the chemisorption of the poison on them. At a constant temperature, the rate of adsorption and the amount of the adsorbed substance depend only on the concentration of the poison in the reaction mixture. In this case, it is more correct to consider the change in the specific activity of the catalyst as a function of the concentration of the poison in solution and not as a function of the poison: catalyst ratio frequently employed. It has been established^{79, 100} that the specific rate of hydrogenation of 3-thiolene 1,1-dioxide in isopropyl alcohol on the 1% Pd/Al₂O₃ catalyst (20 °C, $P = 0.1$ MPa, $c = 0.127$ M) remains constant ($W = 0.2$ mmol min⁻¹ m⁻² Pd) with the concentration of the poison (thiolane) remaining unchanged at 0.5×10^{-3} M and for different ratios (0.5–4) of the number of moles of the poison to the number of gram-atoms of palladium. If this ratio is kept constant at unity and the concentration of thiolane is increased from 0.1×10^{-3} to 1.75×10^{-3} M, then the specific rate of hydrogenation of 3-thiolene 1,1-dioxide falls by an order of magnitude (from 1.2 to 0.15 mmol h⁻¹ m⁻² Pd).

When the specific surface of the catalyst remains constant as a function of time, it is useful to measure not the specific activity of the catalyst but the productivity or degree of conversion of the substrate (if it is less than 100%) in order to obtain an approximate estimate of the resistance to sulfur. The resistance of catalysts to poisoning has been determined in the kinetic region.^{18, 42, 66, 79} For this purpose, the activities of the catalyst in reactions using the pure starting material and the starting material to which a definite amount of poison had been added were compared. A fresh portion of the catalyst was taken for each experiment and the reaction was carried out during the same time interval. In order to determine the resistance of catalysts in the hydrogenation of 3-thiolene 1,1-dioxide to the poisons present in the initial solution and those generated in the course of the process, the experiments were performed for the same catalyst sample, several portions of the substrate being introduced successively into the hydrogenated solution, the composition of which was kept constant. The concentration of the poison or the amount of thiolane 1,1-dioxide for which different catalysts are deactivated to the same level was assumed to be a measure of the resistance to sulfur. This level was as a rule characterised by the ratio W/W_0 , where W is the current reaction rate and W_0 is its initial value.

In the initial stage, the ratio W/W_0 decreases almost linearly as the concentration of the poison introduced or the amount of thiolane 1,1-dioxide formed on hydrogenation increases. Afterwards, the rate of change of the activity decreases and it is finally stabilised at a constant, lower than initial, level. The nonlinear decrease in activity is caused by the inhomogeneity of the catalyst surface and the attainment of the limiting level is due to the establishment of a new stationary state of the catalyst under the influence of the reaction medium. This may be associated with a change in the nature of the active component, for example with the conversion of the metal into the sulfide or with the appearance of steric hindrance in the interaction of the sulfur-containing poison with the active centre of the catalyst.

The results of studies of the resistance of various metals to sulfur in the hydrogenation of 3-thiolene 1,1-dioxide are described below.

Iridium, osmium, ruthenium, and platinum. In the hydrogenation of 3-thiolene 1,1-dioxide, iridium, osmium, ruthenium, and platinum blacks as well as the same metals deposited on γ -Al₂O₃ are unstable and their activity diminishes as the reaction proceeds.^{42, 93} The complete deactivation of 1 g of the catalyst occurs after the formation of between 8 and 42 mmol of thiolane 1,1-dioxide (Table 2).

It has been established for the Ru/Al₂O₃ catalyst that the resistance to sulfur is independent of the hydrogen pressure in the range 0.1–10 MPa and amounts to ~ 40 mmol g⁻¹. The resist-

ance of platinum to sulfur is influenced by the acidity of the hydrogenated solution. Thus, in the hydrogenation of the second portion of 3-thiolene 1,1-dioxide, the initial activity of the same platinum sample decreases by a factor of 3 in a neutral solution and by a factor of 1.2 in a hydrochloric acid solution.⁴⁷

The specific resistances of ruthenium, iridium, and platinum blacks per unit surface are the same as the resistances of these metals deposited on γ -Al₂O₃ (Table 2).

Sulfur dioxide and hydrogen sulfide are strong poisons for ruthenium and platinum.⁴² For complete deactivation of these metals, the hydrogenated solution should contain 0.05×10^{-3} and 0.7×10^{-3} M of hydrogen sulfide respectively or $\sim 0.14 \times 10^{-3}$ M of sulfur dioxide.

Rhodium. Metallic rhodium is relatively stable in the course of the hydrogenation of 3-thiolene 1,1-dioxide: the complete deactivation of 1 g of rhodium black occurs only after the formation of 1330 mmol of thiolane 1,1-dioxide.⁴² The resistance to sulfur referred to unit mass of the catalyst is higher the higher the degree of dispersion of rhodium and the resistance calculated per m² of the metal is independent of the degree of dispersion of the latter (Table 3).

Rhodium is deactivated by sulfur dioxide.^{42, 48, 49} When the hydrogenated solution contains SO₂ at a concentration of 0.08×10^{-3} M, the activity of rhodium black decreases by a factor of 2 and at [SO₂] = 0.125×10^{-3} M the catalyst loses its activity altogether. Divalent sulfur compounds are also poisons for rhodium. For example, when H₂S is introduced at concentrations of 0.6×10^{-3} and 1×10^{-3} M, the activity of rhodium black decreases by 50% and 100% respectively. Treatment of rhodium black with gaseous sulfur dioxide and hydrogen sulfide (20 °C, $P = 0.1$ MPa, $t = 5$ min) reduces sharply its initial activity in the hydrogenation of 3-thiolene 1,1-dioxide (20 °C, $P = 5$ MPa, $c = 0.4$ M). Whereas the rate of formation of thiolane 1,1-dioxide on fresh rhodium is 52.5 mol h⁻¹ g⁻¹, after treatment with gaseous SO₂ and H₂S it decreases to 0.14 and 0.06 mol h⁻¹ g⁻¹ respectively.⁴⁹ When the rhodium catalyst is treated with hydrogen sulfide, its temperature rises to 200 °C, but this effect is absent in the interaction of rhodium with sulfur dioxide. It has been suggested that sulfur dioxide is adsorbed on rhodium associatively, whereas hydrogen sulfide is adsorbed dissociatively.^{42, 49}

The deactivated rhodium catalyst cannot be regenerated by washing with water, acetone, isopropyl alcohol and hydrogen peroxide with subsequent heat treatment in an inert medium or in hydrogen at 100–300 °C. Oxidative treatment of the deactivated rhodium catalyst at 50–300 °C also fails. One of the causes of such failure may be the oxidation of metallic rhodium to the oxide Rh₂O₃, which does not exhibit an activity in the hydrogenation of 3-thiolene 1,1-dioxide (20 °C, $P = 5$ MPa, $c = 0.4$ M, $g_{\text{cat}} = 1.8$ g litre⁻¹, $t = 1$ min). After its reduction with hydrogen at 300 °C for 2 h, the specific surface diminishes from 162 to 9.5 m² g⁻¹ and the metallic rhodium formed greatly accelerates the hydrogenation of 3-thiolene 1,1-dioxide (specific activity 230 mol h⁻¹ g⁻¹).^{48, 93} The XPA spectrum of rhodium black treated with air at 100–500 °C shows lines characteristic of metallic rhodium (2.20, 1.90, 1.345, and 1.146 Å). Rh₂O₃ lines (3.68, 3.62, 2.722, and 2.623 Å) appear in the spectrum of specimens oxidised at 400–500 °C.⁸²

The oxidation-reduction regeneration of rhodium catalysts may be difficult because of the high stability of the surface compounds, the decomposition of which requires severe conditions, in particular the use of high temperatures, which promotes the sintering of the metal. Thus, when the Rh/Al₂O₃ catalyst treated with hydrogen sulfide or sulfur dioxide at 20 °C as well as authentic rhodium sulfide and sulfate deposited on γ -Al₂O₃ are heated in air, the evolution of sulfur dioxide does not begin until 600 °C.

Nickel. The hydrogenation of 3-thiolene 1,1-dioxide has been studied in detail⁵⁷ in the kinetic region on Raney nickel obtained by leaching an alloy containing 53.2 mass % of Al, 44.1 mass % of Ni, and 2.7 mass % of Ti. With increase in contact time, the

reaction rate constant fell (20°C , $P = 4\text{--}5\text{ MPa}$, $c = 0.37\text{ M}$). This may be a consequence of the deactivation of the catalyst. Indeed on successive hydrogenation of several portions of 3-thiolene 1,1-dioxide for a constant composition of the hydrogenated solution, the rate of reaction fell with increase in the amount of thiolane 1,1-dioxide formed.

The rate of hydrogenation is influenced by the composition of the solvent: in thiolane 1,1-dioxide and in the mixture of isopropyl alcohol with 10 mass %–15 mass % of thiolane 1,1-dioxide, the reaction rates differ almost by an order of magnitude (0.83 and $5.42\text{ mol h}^{-1}\text{ g}^{-1}$ respectively). However, the stability of the catalyst is independent of the nature of the solvent and is determined solely by the amount of hydrogenated 3-thiolene 1,1-dioxide. The stability of the catalyst is influenced by the hydrogenation temperature. Thus, when the reaction is carried out at 21 and 25°C ($P = 5\text{ MPa}$, $c = 0.37\text{ M}$), the complete deactivation of 1 g of Raney nickel takes place after the formation of 133 and 75 mmol of thiolane 1,1-dioxide respectively.

The rate of hydrogenation is influenced also by the content of the sulfur dioxide impurity in the solution: at SO_2 concentrations of 0.2×10^{-3} and $40 \times 10^{-3}\text{ M}$, the reaction rates are 0.83 and $0.3\text{ mol h}^{-1}\text{ g}^{-1}$ respectively. The absence of a direct proportionality between the rate and the SO_2 concentration is probably due to the additional formation of sulfur dioxide during the reaction. The linear decrease in the activity of nickel with increase in the amount of hydrogenated 3-thiolene 1,1-dioxide and the independence of the activation energy of the degree of deactivation of the catalyst ($E = 25 \pm 8\text{ kJ mol}^{-1}$) permitted the conclusion that the deactivation of nickel is induced by the decrease in the fraction of the working active surface of the catalyst.⁵⁷

At the end of the hydrogenation of 3-thiolene 1,1-dioxide, the nickel potential is found to be below the hydrogen potential before the reaction, which may be a consequence of the partial dehydrogenation of the surface. The decrease in the stability of the catalysts as a consequence of dehydrogenation may be reduced by carrying out the process in the external diffusion region (in relation to the compound hydrogenated).¹⁰¹ However, the stability of the 50% Ni/Cr₂O₃ nickel catalyst is virtually independent of the region in which the reaction is carried out.^{46,63,69} Thus in the kinetic region (30°C , $P = 2\text{ MPa}$, $c = 0.4\text{ M}$, solution in thiolane 1,1-dioxide), in the external diffusion region in relation to 3-thiolene 1,1-dioxide (35°C , $P = 5\text{ MPa}$, $c = 1\text{ M}$), and in the external diffusion region in relation to hydrogen (20°C , $P = 0.1\text{ MPa}$, $c = 0.2\text{ M}$, solution in isopropyl alcohol), complete deactivation occurred after the formation of 167 , 150 , and 130 mmol of thiolane 1,1-dioxide per gram of the catalyst respectively.

The degree of dehydrogenation can also be diminished by increasing the strength of the bond between hydrogen and the surface, for example by increasing the pH of the medium.³⁹ Thus, in the hydrogenation of 3-thiolene 1,1-dioxide on the nickel-chromium catalyst in solution in isopropyl alcohol at pH 10.4, the anodic shift of the catalyst potential is smaller by 100 mV than at pH 6.5. This indicates a strengthening of the bond between hydrogen and the surface at the high pH. However, this factor does not affect the stability of the catalyst, its deactivation occurring after the formation of $150\text{--}170\text{ mmol}$ of thiolane 1,1-dioxide per gram of the catalyst.

The strengthening of the bond between hydrogen and the surface of the nickel-chromium catalyst is promoted by the addition of 1 mass % of platinum.^{65,67,68} This is indicated by the results of the measurement of the catalyst potentials. After the introduction of 3-thiolene 1,1-dioxide into a neutral solution (20°C , $P = 0.1\text{ MPa}$) the shift of the Ni/Cr₂O₃ potential was $250\text{--}300\text{ mV}$ and that of the (Ni + Pt)/Cr₂O₃ potential was 100 mV . The initial activity of the nickel-chromium catalyst does not change after the addition of 0.1 mass %–4.0 mass % of platinum ($W = 33\text{--}35\text{ mol h}^{-1}\text{ g}^{-1}$). This is explained by the fact that the hydrogenation reaction is limited by the activation of the substrate.¹⁷ The Pt/Cr₂O₃ catalyst exhibits an extremely low activity and a low stability in the hydrogenation of 3-thiolene 1,1-

dioxide. On the other hand, the (Ni + Pt)/Cr₂O₃ specimen is much more stable than the unpromoted specimen. Thus Ni/Cr₂O₃ was fully deactivated after the formation on it of 150 mmol of thiolane 1,1-dioxide per gram of the catalyst, while the deactivation of specimens containing in addition 1 mass % and 4 mass % of platinum required the formation of 260 and 420 mmol g^{-1} of thiolane 1,1-dioxide. The increase in the stability of the (Ni + Pt)/Cr₂O₃ system is probably due to the decrease in the degree of dehydrogenation of the surface as a consequence of the strengthening of the bond between hydrogen and the catalyst. This reduces the rate of interaction of the poison in the starting material with the catalyst and, what is most important, hinders the dissociative adsorption of 3-thiolene 1,1-dioxide with formation of contact poisons.

In the hydrogenation of 3-thiolene 1,1-dioxide to thiolane 1,1-dioxide in isopropyl alcohol, the resistance of Raney nickel to sulfur may be increased by modifying it by adding certain metals.⁵⁹ The stability of modified Raney nickel depends on the Ni : Al ratio in the alloy and on the method used to introduce the additives (in the fusion stage or during the leaching process). In the modification of Raney nickel by the addition of 0.1 mass %–1 mass % of copper, cobalt, chromium, or platinum in the leaching stage, the stability of the catalyst increases by a factor of only 1.1–1.6, whilst after the addition of 0.1 mass %–2 mass % of vanadium or molybdenum the increase is by a factor of 2–3. The addition of molybdenum (1 mass %–12.5 mass %), vanadium (4.7 mass %–14.8 mass %), and zirconium or niobium (1 mass %) to nickel in the fusion stage leads to the formation of a catalyst more stable by a factor of 2–7 than unpromoted Raney nickel (Table 4).

The hydrogenation of 3-thiolene 1,1-dioxide on the nickel catalyst may be complicated by the occurrence of side reactions involving the formation of buta-1,3-diene, sulfur dioxide, butanethiol, and hydrogen sulfide (see above). The activity of the nickel-chromium catalyst in the hydrogenation of 3-thiolene 1,1-dioxide in the kinetic region in the presence of these substances diminishes (30°C , $P = 0.1\text{ MPa}$, $c = 0.85\text{ M}$, solution in thiolane 1,1-dioxide).⁶⁶

Thiolane is a powerful poison for the nickel-chromium catalyst: the initial rate of hydrogenation ($16\text{ mmol h}^{-1}\text{ g}^{-1}$) decreased by a factor of approximately 6 after the introduction of thiolane at a concentration of $4 \times 10^{-3}\text{ M}$ into the hydrogenated solution. However, a further increase in the thiolane concentration does not alter the rate of hydrogenation. The existence of a limit to poisoning by thiolane can be explained by the fact that, in the interaction with the relatively large thiolane molecules (effective size $\sim 60\text{ \AA}$), a proportion of the nickel atoms are protected. Taking into account the size of the thiolane molecule and the Ni–Ni interatomic distance, one may claim that the maximum degree of surface coverage by thiolane does not exceed 50%.¹⁰² The limiting capacity of the nickel-chromium catalyst with respect to thiolane, determined from the adsorption of the latter from solutions in xylene, is $0.17\text{ mmol per gram}$ of the catalyst and is attained at a thiolane concentration of $16 \times 10^{-3}\text{ M}$. In the presence of this content of the poison, the catalyst nevertheless still possesses some activity. Part of the thiolane is probably adsorbed on the surface sites which are not involved in hydrogenation.

Butanethiol at a concentration of $(1\text{--}2) \times 10^{-3}\text{ M}$ hardly affects the activity of the nickel-chromium catalyst presaturated with hydrogen. The rate of hydrogenation on the catalyst which has not been saturated with hydrogen initially diminishes after the addition of butanethiol at a concentration of $\sim 1 \times 10^{-3}\text{ M}$, but, as the reaction proceeds, it increases again and becomes the same as in the absence of the additive. It has been stated¹⁰³ that nickel is reversibly poisoned by phenylmethanethiol. The observed effect can be accounted for by the fact that the thiol is weakly adsorbed on the surface, forming either a Ni–S bond, which is weakened owing to the reduced electron-donating capacity of the sulfur in the thiol,⁴⁰ or a weak Ni–C bond.¹⁰⁴ The thiol weakly bound to

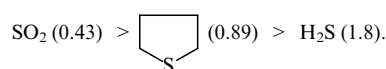
the surface is gradually displaced into the solution by 3-thiolene 1,1-dioxide or hydrogen.⁶⁶

The hydrogen sulfide present in the hydrogenated solution at a low concentration (up to 0.2×10^{-3} M) increases the rate of hydrogenation of 3-thiolene 1,1-dioxide on the nickel-chromium catalyst by a factor of 1.5. However, at a higher concentration ($2.3\text{--}17 \times 10^{-3}$ M) the rate of hydrogenation decreases by a factor of approximately 5.⁶⁶ Similar effects involving the promotion and poisoning of nickel by divalent sulfur compounds have been observed by Kinza *et al.*¹⁰⁵ They were explained by the fact that, as a consequence of the transfer of p electrons of the sulfur atom in hydrogen sulfide to the d band of nickel, the reactant--catalyst bond is loosened. At a low concentration of the sulfur compound, the optimum bond strength, most suitable for hydrogenation, is attained and this increases the rate of reaction. At a high hydrogen sulfide concentration in solution, the promotion effect is overlapped by the effect involving the blocking of the catalyst surface by the sulfur-containing poison and the rate of hydrogenation falls.

Sulfur dioxide is reduced on the nickel-chromium catalyst to hydrogen sulfide at a rate of $2 \text{ mmol h}^{-1} \text{ g}^{-1}$ (30°C , $P = 0.1 \text{ MPa}$, $g_{\text{ct}} = 50 \text{ g}^{-1} \text{ litre}^{-1}$, $[\text{SO}_2] = 9.4 \times 10^{-3} \text{ M}$). When sulfur dioxide is introduced into the hydrogenated solution, the same effects are therefore observed as in the presence of hydrogen sulfide.⁶⁶

Buta-1,3-diene at its concentration in solution of $(0.19\text{--}35) \times 10^{-3} \text{ M}$, increases by a factor of 2 the rate of hydrogenation of 3-thiolene 1,1-dioxide on the nickel-chromium catalyst. In the absence of 3-thiolene 1,1-dioxide, the hydrogenation of buta-1,3-diene is extremely slow and leads to the rapid deactivation of the catalyst, possibly as a consequence of polymerisation. However, the deactivation has been explained⁶⁶ by the interaction of the π electrons of the conjugated system with the d band of nickel *via* the mechanism proposed by Kinza *et al.*¹⁰⁵ At a concentration of $(35\text{--}208) \times 10^{-3} \text{ M}$, buta-1,3-diene induces a small decrease (by a factor of ~ 1.2) of the rate of hydrogenation of 3-thiolene 1,1-dioxide, probably owing to the formation of a butadiene film on the nickel surface or as a consequence of the displacement of part of the substrate from the catalyst by butadiene.

Thus the poisons for the nickel-chromium catalysts are thiolane, hydrogen sulfide, and sulfur dioxide, which can be arranged in the following sequence in terms of their toxicity (the concentration of the poison expressed in mmol litre^{-1} at which the rate of hydrogenation of 3-thiolene 1,1-dioxide decreases by a factor of 2):



For the complete poisoning of the nickel-chromium catalyst, the content of the poison in solution should be $(2.3\text{--}3.9) \times 10^{-3} \text{ M}$. The poisoning of the catalyst is apparently associated with the formation of the Ni-S bond. It was therefore concluded that the above poisons deactivate the same active centres of the catalyst.⁶⁶

The introduction of certain compounds is recommended for the neutralisation of the sulfur dioxide present in the hydrogenated solution.^{53, 106-112} The stability of Raney nickel in the hydrogenation of 3-thiolene 1,1-dioxide increases by a factor of 2-4 after the addition of hydrogen peroxide to a neutral or alkaline ($\text{pH} < 8$) solution.¹¹¹ The hydrogenation of 3-thiolene 1,1-dioxide on massive nickel was carried out in benzene, dioxane, alcohol, and thiolane 1,1-dioxide to which small amounts of the carbonates, hydroxides, and alkoxides of alkali metals or organic amines had been added.⁵³ According to the author's claim, this makes it possible to carry out the process at an elevated temperature and to increase the lifetime of the catalyst. In the presence of added sodium bisulfite or its mixture with sodium hydroxide, at a concentration of 0.5 mass % - 2 mass %, the stability of Raney nickel increases: the additives increase the maximum yield of

thiolane 1,1-dioxide (20°C , $P = 0.1 \text{ MPa}$, $c = 0.3\text{--}0.6 \text{ M}$) from 55% to 85%. The modified nickel ($30\text{--}40^\circ\text{C}$, $P = 10 \text{ MPa}$, $c = 1.4 \text{ M}$, $t = 6.5\text{--}8 \text{ h}$) also works more steadily in the hydrogenation of 3-thiolene 1,1-dioxide in isopropyl alcohol or in thiolane 1,1-dioxide and, its mixture with water (1:1) in the presence of 2 mass % - 4 mass % of pyridine.¹¹² The maximum yield of thiolane 1,1-dioxide in the absence of additives was 87% - 89%, whilst in the presence of pyridine it increased to 100%. 3-Thiolene 1,1-dioxide decomposes on the catalyst which has not been washed free of alkali and polymeric compounds, tentatively polyacrolein, are formed on the surface.¹¹²

However, Mashkina *et al.*⁵⁷ established that the introduction of additives which, according to other data,¹⁰⁶⁻¹¹² are detoxifying agents in relation to the poisons formed during the process (primarily sulfur dioxide), does not allow an increase in the stability of Raney nickel. Thus, in the hydrogenation of 3-thiolene 1,1-dioxide to thiolane 1,1-dioxide in the kinetic region (20°C , $P = 4 \text{ MPa}$, $c = 0.28 \text{ M}$, $[\text{SO}_2] = 39 \times 10^{-3} \text{ M}$), the addition of hydrogen peroxide and sodium, potassium, or ammonium hydroxides did not prevent the poisoning effect of sulfur dioxide (Table 8).

In the successive hydrogenation in the kinetic region of several portions of thoroughly purified 3-thiolene 1,1-dioxide (sulfur

Table 8. The influence of the addition of certain substances on the hydrogenation of 3-thiolene 1,1-dioxide on Raney nickel in thiolane 1,1-dioxide in the presence of sulfur dioxide.⁵⁷

Additive	Content of additive ^a (mass %)	Activity /mmol h ⁻¹ g ⁻¹	Stability /mmol g ⁻¹
[SO ₂] ₀ = 0.2 mass %			
None	—	300	
H ₂ O ₂	0.26	308	
	0.90	200	
NaOH	0.54	366	
	1.47	350	
KOH	0.85	250	
NH ₄ OH	1.2	183	
NaOH +	14.1 +	583	
+ H ₂ O ₂	+ 4.1		
[SO ₂] ₀ = 0.01 mass %			
None	—	830	183
NaOH	0.5	833	100
NaHSO ₃	2.1	664	50
CH ₃ OC ₂ H ₅	1.3	830	250
Ionol	0.4	1000	192
	1.0	835	108
(C ₂ H ₅) ₃ N	0.8	830	183

^a Relative to 3-thiolene 1,1-dioxide.

dioxide concentration $0.14 \times 10^{-3} \text{ M}$) under the conditions of a constant composition of the hydrogenated solution, 1 g of nickel was fully deactivated after the formation of 183 mmol of thiolane 1,1-dioxide. Nor did the stability of the catalyst change after the addition to the hydrogenated solution of sodium hydroxide, ethyl methyl ketone, ionol, or triethylamine, while the addition of sodium bisulfite and large amounts of ionol actually reduced the rate of hydrogenation of 3-thiolene 1,1-dioxide by a factor of 2-3. Under these conditions, the additives did not influence the initial activity of the catalyst (Table 8).

The nickel catalyst deactivated by sulfur compounds is difficult to regenerate.^{113, 114}

Palladium. Like other Group VIII metals, palladium is deactivated in the course of the hydrogenation of 3-thiolene 1,1-dioxide. On the 2% Pd/SiO₂ catalyst, the yield of thiolane 1,1-

dioxide falls from 100% to 80% after the formation of 250 mmol of the latter on 1 g of the catalyst (20 °C, $P = 7.8$ MPa, $c = 1.4$ M, space velocity 4.5 h).¹¹⁵

After the completion of the hydrogenation of one portion of 3-thiolene 1,1-dioxide on the 5% Pd/BaSO₄ catalyst (30 °C, $P = 0.1$ MPa, $c = 0.07$ M), the potential of the latter becomes less than the reversible hydrogen potential (630–640 mV), which indicates partial poisoning of the surface.⁴⁷ On repeated hydrogenation, the initial activity of the catalyst, amounting to 0.92 mol h⁻¹ g⁻¹, decreases by a factor of 4. It was established that this is associated with the deactivation of the catalyst and not with the accumulation of the reaction product in solution.

At a low temperature (10–30 °C), the stability of palladium-containing catalysts is determined solely by the amount of hydrogenated 3-thiolene 1,1-dioxide and not by the rate of its conversion.^{42,93} For this reason, changes in the hydrogen pressure, the nature of the solvent, and in the content of the substrate in the latter do not affect the stability of the catalyst. However, with increase in temperature, the stability falls at unchanged pressure and 3-thiolene 1,1-dioxide concentration. Thus the stabilities of the 5% Pd/Al₂O₃ catalyst at $P = 5$ MPa, $c = 0.4$ M, and temperatures of 20, 30, 50, 70, and 80 °C were respectively 1040, 808, 433, 30, and 8 mmol g⁻¹. This is associated with the increase in the rate of decomposition of 3-thiolene 1,1-dioxide as the temperature rises with formation of products which poison palladium.

The degree of deactivation of the palladium-containing catalyst in the hydrogenation of 3-thiolene 1,1-dioxide depends on the purity of the hydrogenated solution. Thus, when the sulfur dioxide contents were 0.014×10^{-3} , 0.029×10^{-3} , and 0.04×10^{-3} M, 1 g of the 5% Pd/Al₂O₃ catalyst was fully deactivated after the formation on the latter of 416, 833, and 1833 mmol of thiolane 1,1-dioxide respectively.⁴²

An increase in the palladium content increases the stability of the catalyst. The nature of the carrier (aluminium oxide, aluminosilicate, silicon dioxide, activated charcoal) also exerts a definite influence. Palladium deposited on γ -Al₂O₃ (Table 5) is the most stable.^{77,83,93} It was shown above that the nature of the carrier and the surface concentration of palladium influence the degree of dispersion and activity of the latter. It was found that the more accessible becomes the palladium surface the greater the increase not only in the activity but also in the stability of the catalyst. The factors which tend to increase the activity per unit mass of the catalyst (a large area of the carrier, a high palladium content, the addition of boron, manganese, or platinum group metals, activation of the catalyst by air, and the optimum preparation procedure) have a favourable effect also on the stability of the palladium-containing catalyst (Tables 5–7).

Thus an increase in the stability of the palladium catalyst is promoted by a decrease in the hydrogenation temperature, by an increase in the accessible surface of the metal, and by the thorough elimination of sulfur dioxide from 3-thiolene 1,1-dioxide. Nevertheless, this does not fully protect the catalyst against deactivation.

The deactivation of palladium-containing catalysts is caused by their poisoning by tetravalent and divalent sulfur compounds.

Sulfur dioxide is capable of interacting with palladium. After the treatment of palladium with gaseous SO₂ (20 °C, $P = 0.1$ MPa, $t = 5$ min), the specimen contains 0.4 mass % of sulfur. Sulfur dioxide is adsorbed on palladium-containing catalysts (1 mass %–8 mass % of Pd on γ -Al₂O₃, AlSi, SiO₂, or C) from solution in isopropyl alcohol with added 10 mass % of thiolane 1,1-dioxide at a rate of 0.006–0.012 mmol h⁻¹ m⁻² Pd.^{18,42} SO₂ is rapidly adsorbed on palladium films even at –80 °C. For surface coverages up to 0.8, dissociative chemisorption takes place, but part of the sulfur dioxide is adsorbed without decomposition. The fraction of the associatively adsorbed SO₂ increases with increase in the degree of surface coverage. Sulfur dioxide may be removed by evacuation.¹¹⁶

After the desorption of sulfur dioxide, the activity of the palladium catalyst in the hydrogenation of 3-thiolene 1,1-dioxide

is restored to the previous level. The addition of sulfur dioxide to the 3-thiolene 1,1-dioxide solution diminishes the activity of palladium. It follows from the analysis of the poisoning isotherms^{18,42} that, when the SO₂ content is 0.18×10^{-3} M, the rate of reaction diminishes by a factor of 2, while at its concentration of 0.28×10^{-3} M complete deactivation of the catalyst takes place (20 °C, $P = 5$ MPa, $c = 0.4$ M). The activity of the 5% Pd/Al₂O₃ catalyst with adsorbed sulfur dioxide in the hydrogenation of 3-thiolene 1,1-dioxide (20 °C, $P = 5$ MPa, $c = 0.4$ M) is 15 times smaller than that of the initial specimen (13.3 and 0.03 mol h⁻¹ g⁻¹ respectively).^{18,42} The stability of the catalyst therefore depends greatly on the purity of 3-thiolene 1,1-dioxide. Sulfur dioxide is formed to some extent also in the hydrogenation of 3-thiolene 1,1-dioxide because of the ready dissociation of the latter.

It has been established¹¹⁷ that sulfur dioxide, which is a powerful π -electron acceptor, forms a dative bond with the central metal atom of the complex catalyst as a result of electron transfer from the metal to the unoccupied orbital of sulfur. It may be that this is true also of the solid metallic catalyst. The ability of palladium on which sulfur dioxide has been adsorbed to activate hydrogen may be retained under these conditions. Thus palladium treated with sulfur dioxide at 20 °C adsorbs hydrogen, but its activity in the hydrogenation of 3-thiolene 1,1-dioxide reduced.^{18,116} This is apparently induced by the decrease in the dative capacity of palladium, which hinders the formation of a π -olefin complex ensures the activation of the C=C bond of the sulfone.

In the hydrogenation of 3-thiolene 1,1-dioxide contaminated by sulfur dioxide, the palladium-containing catalyst is deactivated and cannot be regenerated either by washing with solvents (water, acetone, and isopropyl alcohol), or by oxidation with hydrogen peroxide, or by exposure to a stream of an inert gas at 200–300 °C. The regeneration is achieved only as a result of the reduction of the specimen with hydrogen at 300 °C for 6 h.⁸⁸

In a hydrogen atmosphere, the sulfur dioxide adsorbed on palladium is reduced to hydrogen sulfide and the rate of hydrogenation is 0.3 mol min⁻¹ g⁻¹ {20 °C, $P = 0.1$ MPa, solution in isopropyl alcohol, [SO₂] = 0.1 M} and increases with increase in pressure. It was therefore concluded²² that the change in the catalytic properties of palladium is associated with the effect on the latter by the hydrogen sulfide arising during the reduction of sulfur dioxide.

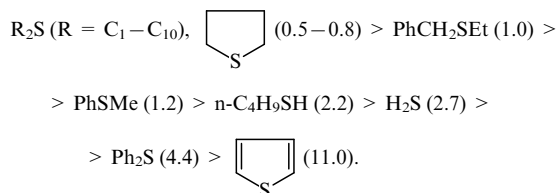
Hydrogen sulfide also readily interacts with palladium. When the palladium-containing catalyst is treated with gaseous H₂S (20 °C, $P = 0.1$ MPa, $t = 5$ min), the specimen heats up to 200 °C. After such treatment, the catalyst contains 5 mass % of sulfur.⁴² The adsorption of hydrogen sulfide on palladium is irreversible. The rate of hydrogenation of 3-thiolene 1,1-dioxide on the sulfided specimen is 80 times lower than on the fresh catalyst: at 20 °C, $P = 5$ MPa, and $c = 0.4$ M, it is respectively 13.3 and 0.16 mol h⁻¹ g⁻¹. The introduction of hydrogen sulfide into the solution also reduces the rate of formation of thiolane 1,1-dioxide; at [H₂S] = 0.1×10^{-3} M, the activity decreases by a factor of 2 and at [H₂S] = 0.2×10^{-3} M the catalyst is fully deactivated. The complete deactivation of catalysts of different composition requires ~ 0.05 mmol of hydrogen sulfide per m² of palladium.

In the interaction of hydrogen sulfide with metallic palladium, palladium sulfide is probably formed even at room temperature. Like other metal sulfides, it is appreciably less active than the metal itself (see below).

The regeneration of Pd/Al₂O₃ poisoned with hydrogen sulfide can be achieved only after its reduction with hydrogen at 300 °C for 6 h.

Organic compounds of divalent sulfur also deactivate metallic palladium. The influence of various divalent sulfur compounds on the activity of the 4.7% Pd/Al₂O₃ catalyst in the hydrogenation of 3-thiolene 1,1-dioxide (20 °C, $P = 5$ MPa, $c = 0.4$ M, $t = 0.5$ –1 min) has been investigated.¹¹⁸ It was found that the

stability of the catalyst, estimated as the amount of sulfur required for the complete deactivation of 1 g of the catalyst (α_S), depends on the structure of the sulfur compound. In terms of their toxicity in relation to the catalysts of the hydrogenation of 3-thiolene 1,1-dioxide, the compounds can be arranged in the following sequence corresponding to the changes in the electron-donating capacity of the sulfur entering into their composition (the values of α_S expressed in mg-atom g⁻¹ are indicated in brackets):



A linear relation has been established between the Taft inductive constants and the toxicity of dialkyl sulfides, which indicates the formation of a surface donor–acceptor complex $\text{Pd} \leftarrow \text{S}^{14, 118}$

There exists the view that the resistance of metallic palladium to sulfur may increase when it is deposited on an acidic carrier (a zeolite or $\gamma\text{-Al}_2\text{O}_3$ with added boron) or on activated charcoal.^{119–121} In order to elucidate the contribution of the carrier to the resistance of palladium to the poisoning effect of divalent sulfur compounds, a study has been made^{79, 122} of the hydrogenation of 3-thiolene 1,1-dioxide with added (0.05–5.0) $\times 10^{-3}$ M thiophene and thiolane on metallic palladium deposited on aluminium oxide, an aluminosilicate, silicon dioxide, activated charcoal, and zeolites. In order to avoid the distortion of the sulfur resistance data by effects due to the occurrence of side processes, the authors confined themselves to the measurement of the initial activity, which was inferred from the rate of absorption of hydrogen at the beginning of the stationary section on the kinetic curves (20 °C, $P = 0.1$ MPa, $c = 0.127$ M, conversion 25%–50%). The relative change from the initial rate of hydrogenation in the presence of the poison (W/W_0), determined from the poisoning isotherms, was adopted as the criterion of the resistance of the catalyst to sulfur. In the absence of the poison, the hydrogenation on all the catalysts investigated occurred at a high rate and with 100% yield of thiolane 1,1-dioxide. The rate of reaction remained constant up to the absorption of $\sim 70\%$ of the theoretically required amount of hydrogen and was independent of the size of the catalyst sample ($g_{\text{cat}} = 0.5\text{--}2.5$ g litre⁻¹). The catalysts differed as regards their activities referred to unit mass of the specimen, but the activities calculated per unit surface of the metal were approximately the same (Table 9). The introduction of thiophene and thiolane into the reaction mixture reduced the rate of hydrogenation, the fall being most marked at a poison concentration up to 0.2×10^{-3} M. At higher concentrations, the rate of decrease in the activity fell and at a poison concentration in excess of 2×10^{-3} M the catalyst was fully poisoned. At a concentration $> 1.5 \times 10^{-3}$ M the toxicity of thiolane is higher by a factor of 1.5–3.0 than that of thiophene, but at a lower concentration their toxicities are virtually the same.

Palladium black and palladium deposited in an amount of 1 mass % Al_2O_3 , AlSi , SiO_2 or C have similar resistances to sulfur: a twofold decrease in activity occurs in all cases at a thiolane concentration of $\sim 0.06 \times 10^{-3}$ M, i.e. the nature of the carrier does not affect the stability of the catalyst. At a constant concentration of the poison, the values of W/W_0 for supported catalysts with different palladium contents are virtually the same and close to the corresponding value for palladium black. Since the specific surfaces of the test specimens differed by approximately one order of magnitude, one may conclude that the degree of dispersion of palladium does not affect the stability of the catalyst in relation to the poisoning effect of divalent sulfur compounds. experiments on the hydrogenation of 3-thiolene 1,1-dioxide with added thiolane

Table 9. The resistance of various palladium-containing catalysts to sulfur in the hydrogenation of 3-thiolene 1,1-dioxide (20 °C, $P = 0.1$ MPa, $c = 0.127$ M).^{79, 122}

Catalyst	S_{sp} /m ² g ⁻¹ Pd	Rate of hydrogena- tion of pure substrate		[Poison] ^c	W/W_0 (%)	
		see ^a	see ^b		thio- lane	thio- phene
Pd black	40	1.0	2.5	0.1	42	—
	40	1.0	2.5	0.24	20	—
0.1% Pd/Al ₂ O ₃	380	17.4	4.9	0.24	14	22
0.5% Pd/Al ₂ O ₃	300	14.7	5.2	0.78	8	12
1% Pd/Al ₂ O ₃	260	10.2	4.2	0.24	18	24
	260	10.2	4.2	0.78	5	12
	260	10.2	4.2	0.05	53	46
	260	10.2	4.2	0.10	36	27
	260	10.2	4.2	0.15	27	26
	260	10.2	4.2	0.50	9	22
0.1% Pd/SiO ₂	220	4.6	2.2	0.24	13	20
0.5% Pd/SiO ₂	130	4.2	3.4	1.2	4	21
1% Pd/SiO ₂	67	1.6	2.6	0.24	12	—
	67	1.6	2.6	1.2	4	7
0.2% Pd/AlSi	140	3.7	2.8	0.45	5	22
0.5% Pd/AlSi	65	2.3	3.7	1.2	4	10
1% Pd/AlSi	75	2.2	3.1	0.45	8	—
	75	2.2	3.1	1.2	3	19
1% Pd/C	165	5.8	3.7	0.5	8	21
5% Pd/C	84	2.4	3.1	1.2	5	9
1% Pd/NaHY:						
7.8% Na	—	0.5	—	0.15	66	—
1.5% Na	—	0.4	—	0.15	64	—
0.9% Na	—	0.5	—	0.15	57	72
	—	0.5	—	1.0	19	17

^a Expressed in (mmol H₂) min⁻¹ (g-atom Pd)⁻¹. ^b Expressed in (mmol H₂) min⁻¹ m⁻² Pd. ^c Expressed in mmol litre⁻¹.

showed that the 1% Pd/HNaY catalyst has a low activity (Table 9), but at a poison concentration of $(0.15\text{--}2.0) \times 10^{-3}$ M the quantity W/W_0 on this specimen is approximately twice as high as on other supported palladium catalysts. This is associated with the partial adsorption of thiolane on the zeolite. However, the zeolite carrier does not fully protect metallic palladium against poisoning and, when thiolane is introduced into the solution at a concentration of 2.5×10^{-3} M, the ratio W/W_0 is only 3%. The different acidities of the palladium-zeolite catalyst containing 0.9 mass %–7.8 mass % of sodium do not affect their resistance to sulfur. The acid centres of the zeolite framework influence the electronic state of palladium, but this is hardly reflected in its resistance to poisoning by divalent sulfur compounds. The results failed to confirm the hypothesis^{119–121} that the deposition of palladium on an acid carrier or charcoal significantly protects it against poisoning by sulfur compounds.

Thus, during the hydrogenation of 3-thiolene 1,1-dioxide, metallic palladium is deactivated by various sulfur compounds. At a low temperature, the poisons in relation to palladium are sulfur dioxide as well as the hydrogen sulfide appearing when the latter is hydrogenated, while at a high temperature organic divalent sulfur compounds are also formed in addition during the process.

The poisoning of metallic palladium by sulfur-containing impurities may be diminished by introducing acid or alkaline additives into the hydrogenated solution.¹²³ Thus, in the hydrogenation of 2-thiolene 1,1-dioxide in a neutral solution in isopropyl alcohol (20 °C, $P = 0.1$ MPa, $c = 0.127$ M), the activity of the 2.5% Pd/ Al_2O_3 catalyst decreases by a factor of 2 following the addition of thiolane at a concentration of 0.1×10^{-3} M. On

the other hand, in the presence of KOH at a concentration of $(0.25-2.5) \times 10^{-3}$ M, the concentration of thiolane required to achieve this effect is $(0.6-1.25) \times 10^{-3}$ M, *i.e.* the resistance of the catalyst to sulfur increases approximately by an order of magnitude. The strength of the bond between hydrogen and the surface probably increases in an alkaline medium and this hinders the chemisorption of thiolane on the active centres. The stability of the same catalyst in the hydrogenation of 2-thiolene 1,1-dioxide in isopropyl alcohol containing an admixture of sulfur dioxide increases by a factor of 2 after the acidification of the solution with hydrochloric acid (0.25×10^{-3} M). It may be that the catalytic poison is the hydrogen sulfide evolved on reduction of sulfur dioxide. Its interaction with palladium leads to the formation of palladium sulfide, while hydrochloric acid ruptures the Pd-S bond.¹²³ Alkali is introduced into the 3-thiolene 1,1-dioxide solution in order to neutralise sulfur dioxide.

The activity of the 2.5% Pd/Al₂O₃ catalyst in the presence of 0.1×10^{-3} M SO₂ in a neutral solution is lower by a factor of 2 than in the hydrogenation of pure 3-thiolene 1,1-dioxide. In the presence of $(0.25-2.5) \times 10^{-3}$ M potassium hydroxide, the poisoning of the catalyst to the same level requires the introduction into the solution of 0.2–0.4 mmol of SO₂ per litre, *i.e.* the stability of the catalyst increases by a factor of 2–4.¹²³ In the hydrogenation of 3-thiolene 1,1-dioxide thoroughly freed from sulfur poisons, an increase in the basicity of the medium, for example by the introduction into the latter of KOH at a concentration of 2.25×10^{-3} M, also tends to increase the stability of palladium, since alkali neutralises the sulfur dioxide formed as a result of the partial decomposition of the substrate.⁴² After the introduction of 0.5 mass % of potassium hydroxide into the 2% Pd/Al₂O₃ catalyst, its stability increases by a factor of two.^{89,93} The stability of the 5% Pd/Al₂O₃ catalyst increases by a factor of 2.5–3.5 also when alkaline adsorbents (the NaY zeolite, Al₂O₃, or SiO₂, all containing 5 mass % of potassium) are added to the solution.^{42,93} However, the activity of palladium-containing catalysts in a basic medium is lower than in a neutral medium. Thus the rate of hydrogenation of 3-thiolene 1,1-dioxide (20 °C $P = 5$ MPa, $c = 0.4$ M) on 4.5% Pd/Al₂O₃ in a neutral medium is $500 \text{ mol h}^{-1} \text{ g}^{-1}$, while after the addition of 0.01 mass % NaOH it is $150 \text{ mol h}^{-1} \text{ g}^{-1}$.⁴²

A more detailed study confirmed^{22,93} that the rate of hydrogenation of 2- and 3-thiolene 1,1-dioxides diminishes in alcoholic solutions (Table 10). At atmospheric pressure, the rate of hydrogenation in isopropyl alcohol {20 °C, [KOH] = $(0.1-10) \times 10^{-3}$ M} and 1-butanol {20 °C, [KOH] = $(13-150) \times 10^{-3}$ M} decreases in proportion to the concentration of potassium hydroxide raised to the power 0.5. If the reaction is carried out in isopropyl alcohol (to which 10% of thiolane 1,1-dioxide has been added) at an elevated hydrogen pressure (5 MPa), the above relation holds only for a NaOH concentration $< 2.3 \times 10^{-3}$ M while at a higher sodium hydroxide concentration the rate of decrease in the rate of hydrogenation of thiolene 1,1-dioxide diminishes.

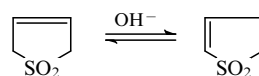
The decrease in the activity of metallic palladium in the hydrogenation of 3-thiolene 1,1-dioxide in an alkaline medium may be induced by various causes. In principle, one cannot rule out the possibility of the blocking of the active centres of the catalyst by the products of the alkaline cleavage of thiolene 1,1-dioxide or thiolane 1,1-dioxide, but such cleavage occurs at an appreciable rate only on refluxing in an aqueous alkaline medium.¹²⁴ The second cause may be the increase in the alkaline medium of the strength of the bond between hydrogen and palladium.³⁹ The hydrogenation of 3-thiolene 1,1-dioxide on metallic catalysts at atmospheric pressure is limited by the activation of hydrogen,¹⁷ so that the strengthening of its bond with palladium may decrease the rate of reaction. With increase in pressure, the mechanism of the hydrogenation of 3-thiolene 1,1-dioxide changes and a strengthening of the bond between hydrogen and the surface therefore has a smaller effect on the activity of the catalyst.

Table 10. The influence of the concentration of alkali on the activity of the Pd/Al₂O₃ catalysts in the hydrogenation of 2- and 3-thiolene 1,1-dioxides.²²

2.5% Pd/Al ₂ O ₃ , 20 °C, $P = 0.1$ MPa, $\bar{d} = 0.4$ M, isopropyl alcohol		4% Pd/Al ₂ O ₃ , 20 °C, $P = 5$ MPa, $\bar{d} = 0.4$ M, isopropyl alcohol		2% Pd/Al ₂ O ₃ , 70 °C, $P = 0.1$ MPa, $\bar{d} = 0.13$ M, 1-butanol	
[KOH] ^a	$10^2 W^b$	[KOH] ^a	$10^2 W^b$	[KOH] ^a	$10^3 W^b$
0	125	0	1541	0	70
0.1	110	0 ^c	1667	2 ^c	59
0.25	98	0.3	1500	10 ^c	53
0.5	92	0.5 ^c	933	13	50
1.5	75	1.0	830	40	35
2.5	68	0.9 ^c	833	65	24
3.0	62	2.3	575	80 ^c	22
4.5	50	2.2 ^c	592	100	16
5.0	41	23	267	130	13
10.0	29	112	150	150	8

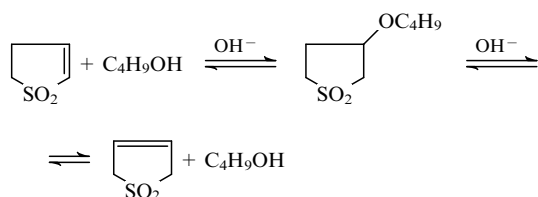
^a Expressed in mmol litre⁻¹. ^b Expressed in mol h⁻¹ g⁻¹. ^c Hydrogenation of 2-thiolene 1,1-dioxide. In the remaining cases, the hydrogenation of 3-thiolene 1,1-dioxide is meant.

The rate of hydrogenation of 3-thiolene 1,1-dioxide in an alkaline medium may also change owing to a transformation of the substrate unrelated to the catalytic hydrogenation. Thus the double bond in the 3-thiolene 1,1-dioxide ring may migrate under the influence of bases in alcoholic solutions with formation of 2-thiolene 1,1-dioxide.

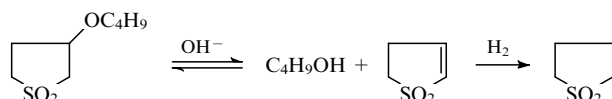


The isomerisation in the presence of an alkaline agent occurs even at room temperature and is accelerated on heating.⁶ However, the conversion of 3-thiolene 1,1-dioxide into 2-thiolene 1,1-dioxide cannot be regarded as the cause of the decrease in the rate of formation of thiolane 1,1-dioxide in an alkaline medium in view of the following considerations. 2-Thiolene 1,1-dioxide is known to be hydrogenated at a high rate in a neutral medium.¹ Under comparable conditions, the rate of formation of thiolane 1,1-dioxide from 2-thiolene 1,1-dioxide is actually somewhat higher than the rate of its formation from 3-thiolene 1,1-dioxide. Thus, on the 2.5% Pd/Al₂O₃ catalyst in isopropyl alcohol, the rates of hydrogenation of 3- and 2-thiolene 1,1-dioxides are respectively 1.12 and 1.33 mol h⁻¹ g⁻¹ at 20 °C, $P = 0.1$ MPa, and $c = 0.4$ M and 3.8 and 4.5 mol h⁻¹ g⁻¹ at 20 °C, $P = 5$ MPa, and $c = 0.13$ M. Under the conditions of the hydrogenation of 2-thiolene 1,1-dioxide in a neutral medium at 20 °C, the palladium catalyst works more steadily than in the hydrogenation of 3-thiolene 1,1-dioxide: the initial rate of hydrogenation of 3-thiolene 1,1-dioxide on a 2.5% Pd/Al₂O₃ specimen, amounting to 12 mol h⁻¹ g⁻¹ decreases to 0.01 mol h⁻¹ g⁻¹ after the formation of 1000 mmol of thiolane 1,1-dioxide per gram of the catalyst, while 2-thiolene 1,1-dioxide is hydrogenated virtually at a constant rate of 12–14 mol h⁻¹ g⁻¹ (20 °C, $P = 5$ MPa, $c = 0.4$ M).²² This is probably due to the fact that 2-thiolene 1,1-dioxide is predisposed to decompose with elimination of sulfur dioxide, which is a poison for palladium. In an alkaline medium, the rate of hydrogenation of 2-thiolene 1,1-dioxide on 2.5% Pd/Al₂O₃ decreases in proportion to the concentration of potassium hydroxide raised to the power 0.5, *i.e.* as happens in the hydrogenation of 3-thiolene 1,1-dioxide (Table 10). One may therefore conclude that the isomerisation of 3-thiolene 1,1-dioxide to 2-thiolene 1,1-dioxide does not decrease the rate of its hydrogenation in alkaline alcoholic solutions.

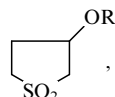
The isomerisation of 3-thiolen 1,1-dioxide to 2-thiolen 1,1-dioxide in primary and secondary alcohols is accompanied by the addition of the alcohol to the double bond activated by the electron-accepting sulfonyl group in the ring. This results in the formation of 3-alkoxythiolane 1,1-dioxides (sulfolanyl esters).⁶ For example, 3-butoxythiolane 1,1-dioxide is formed in butanol.



The reaction is reversible, the content of 3-butoxythiolane 1,1-dioxide amounting to $94\% \pm 2\%$ in the presence of primary alcohols in the equilibrium mixture and to $88\% \pm 2\%$ in the presence of secondary alcohols. In an alkaline solution, 3-alkoxythiolane 1,1-dioxide may decompose with formation of 2-thiolen 1,1-dioxide. This reaction is also reversible.⁶ However, if it is carried out under a hydrogen atmosphere in the presence of a hydrogenation catalyst, then the 2-thiolen 1,1-dioxide formed is hydrogenated and this shifts the equilibrium towards the formation of elimination products.



The occurrence of the above reactions results in the complete conversion of 3-thiolen 1,1-dioxide into thiolane 1,1-dioxide. The possibility of this transformation in the presence of 2.5% Pd/Al₂O₃ has been established in the hydrogenation of authentic 3-alkoxythiolane 1,1-dioxides having the general formula



where $R = C_1 - C_{12}$ ($20 - 85^\circ\text{C}$, $P = 0.1 - 5\text{ MPa}$, $c = 0.06 - 1.4\text{ M}$, $[\text{KOH}] = 0 - 1.42\text{ M}$).¹²⁵ 3-Butoxythiolane 1,1-dioxide is the most reactive. Its hydrogenation takes place in alkaline alcoholic (isopropyl alcohol and *tert*-butyl alcohol), aqueous, and thiolane 1,1-dioxide solutions. In the absence of alkali the rate of reaction is very low. The quantitative yield of thiolane 1,1-dioxide is attained in an aqueous alkaline solution at an elevated temper-

ature and a high content of alkali. The rate of formation of thiolane 1,1-dioxide in the presence of 2.5% Pd/Al₂O₃ from 3-butoxythiolane 1,1-dioxide is much lower than the rate of its formation from 3-thiolen 1,1-dioxide in a neutral medium (Table 11). With increase in temperature from 20 to 85°C , the rate of formation of thiolane 1,1-dioxide from the ether increases, the activation energy being $25 \pm 4\text{ kJ mol}^{-1}$. The rate of reaction depends little on the hydrogen pressure: when it increases from 0.1 to 5 MPa, the rate increases by a factor of 1.3. In an aqueous alkaline solution, the rate of reaction of 3-butoxythiolane 1,1-dioxide initially increases in proportion to its concentration (up to 0.1 M) and then (at a concentration up to 1.5 M) remains constant. The rate of reaction is proportional to the concentration of potassium hydroxide raised to the power 0.5 [for $[\text{KOH}] = 0.013 - 0.89\text{ M}$]. Overall, the rate of formation of thiolane 1,1-dioxide from 3-butoxythiolane 1,1-dioxide is described by the equation

$$W = kc_1^n c_2^{0.5} P^{0.2},$$

where c_1 and c_2 are the concentrations of 3-butoxythiolane 1,1-dioxide and potassium hydroxide respectively, P is the hydrogen pressure, k is the reaction rate constant, and $n = 0$ or 1.

In the presence of alkali, the initial rates of hydrogenation of authentic 2-thiolen 1,1-dioxide and 3-butoxythiolane 1,1-dioxide are of the same order of magnitude. For example, at 85°C , $P = 0.1\text{ MPa}$, $c = 0.127\text{ M}$, and $[\text{KOH}] = 0.89\text{ M}$, they are respectively 32 and $12\text{ mmol h}^{-1}\text{ g}^{-1}$. This observation and the fact that the rate of reaction depends little on the hydrogen pressure permit the conclusion that the formation of thiolane 1,1-dioxide from 3-butoxythiolane 1,1-dioxide is limited by the elimination of the alcohol and not by the reduction of the 2-thiolen 1,1-dioxide formed.¹²⁵

In the hydrogenation of 2- and 3-thiolen 1,1-dioxides as well as 3-butoxythiolane 1,1-dioxide in alcoholic solutions, the rates of formation of thiolane 1,1-dioxide on the 2.5% Pd/Al₂O₃ catalyst are similar (Table 11). One may therefore postulate that the conversion of 3-thiolen 1,1-dioxide in alcoholic alkaline solutions proceeds *via* stages involving isomerisation and addition of the alcohol to the 2- and 3-thiolen 1,1-dioxides with formation of alkoxythiolane 1,1-dioxide and its subsequent hydrogenation to thiolane 1,1-dioxide. In order to attain an acceptable rate of formation of thiolane 1,1-dioxide, the hydrogenation must be carried out at an elevated temperature.

During the hydrogenation of 2- and 3-thiolen 1,1-dioxides and 3-butoxythiolane 1,1-dioxide on 2.5% Pd/Al₂O₃ at atmospheric pressure and a temperature in excess of 70°C , the catalyst is

Table 11. Hydrogenation of 2- and 3-thiolen 1,1-dioxides and 3-butoxythiolane 1,1-dioxide on aluminopalladium catalysts at $P = 5\text{ MPa}$.²²

Catalyst	Solvent	Compound hydrogenated	Content in initial mixture /M		$T/^\circ\text{C}$	$10^3 W / \text{mol h}^{-1}\text{ g}^{-1}$
			Substrate	KOH		
2.5% Pd/Al ₂ O ₃	Isopropyl alcohol	3-Thiolen 1,1-dioxide	0.4	0	20	11 670
		"	0.13	0	20	3750
		"	0.04	0	20	1250
		2-Thiolen 1,1-dioxide	0.4	0	20	12 840
		"	0.13	0	20	4500
		"	0.04	0	20	1500
	Butanol	3-Thiolen 1,1-dioxide	0.53	0	85	8.3
		"	0.53	0.45	87	12.0
		2-Thiolen 1,1-dioxide	0.60	0.45	87	12.5
		3-Butoxythiolane 1,1-dioxide	0.60	0.45	87	13.3
	Butanol	3-Thiolen 1,1-dioxide	0.04	0	100	0.67
		"	0.04	0.45	100	1.0
		2-Thiolen 1,1-dioxide	0.04	0	100	0.83
		3-Butoxythiolane 1,1-dioxide	0.04	0.45	100	1.5

rapidly deactivated despite the high content of alkali in the solution. For example, at 70–85 °C, $[\text{KOH}] = 0.45\text{--}0.89\text{ M}$, and $c = 0.13\text{ M}$, the rate of reaction in an alkaline solution is a maximum in the first minute and then falls sharply (by an order of magnitude).^{22, 125} The rate of formation of thiolane 1,1-dioxide from portions of the substrate introduced successively into the solution on the same catalyst sample (for a constant composition of the solution) does not remain constant. The amount of thiolane 1,1-dioxide formed on 1 g of the catalyst before the decrease in the initial activity by a factor of 20 is independent of the substrate concentration and amounts to $(2\text{--}5) \times 10^{-3}\text{ M}$. At an elevated hydrogen pressure (5 MPa), the catalyst works more steadily: its initial activity does not decrease after the formation of $\sim 400\text{ mmol}$ of thiolane 1,1-dioxide per gram of the catalyst.

The dependence of the stability of metallic palladium on the hydrogen pressure is determined by the ratio of the rates of isomerisation and hydrogenation of 2-thiolene 1,1-dioxide. At atmospheric pressure, the rate of hydrogenation is relatively low and 2-thiolene 1,1-dioxide isomerises to a large extent to 3-thiolene 1,1-dioxide, which is a source for the formation of catalytic poisons. At an elevated pressure, the contribution of the isomerisation process falls since the rate of hydrogenation increases markedly. The significance of the presence of 3-thiolene 1,1-dioxide in the hydrogenated solution for the deactivation of palladium has been confirmed also by experiments on hydrogenation at elevated temperatures, which promote its dissociation. Thus the rate of formation of thiolane 1,1-dioxide from 3-thiolene 1,1-dioxide on the 5% $\text{Pd}/\text{Al}_2\text{O}_3$ catalyst in isopropyl alcohol ($P = 5\text{ MPa}$, $c = 0.53\text{ M}$, conversion 70%) increases from 10 to $54\text{ mol h}^{-1}\text{ g}^{-1}$ with increase in temperature from 8 to 50 °C. At 70–85 °C, it falls sharply, reaching values from 0.4 to $0.01\text{ mol h}^{-1}\text{ g}^{-1}$, since the catalyst is fully deactivated.⁹³

The sulfur dioxide evolved on decomposition of 3-thiolene 1,1-dioxide, is readily reduced in the presence of the palladium catalyst to hydrogen sulfide, which interacts with metallic palladium. Thermodynamic calculations indicate a high probability of the formation of palladium sulfide under these conditions. This process proceeds at a low temperature and accelerates when the latter is increased.¹²⁶ It has been established experimentally that metallic palladium is fully converted into palladium sulfide after treatment with hydrogen sulfide at 200 °C for 30 min.¹⁹ On the other hand, thermodynamic calculations for the $\text{PdS} + \text{H}_2 \rightleftharpoons \text{Pd} + \text{H}_2\text{S}$ system and experimental studies by the XPS and thermostimulated exoelectron emission methods^{16, 127} indicate the possibility of the partial reduction of PdS to metallic palladium (and Pd_2S) at moderate temperatures. However, the reduction of palladium sulfide by hydrogen is much slower than the conversion of metallic palladium into the sulfide: at 200 °C, the degree of reduction is 2% and 83% after 1 and 10 h respectively.¹⁹ One may therefore assume that the catalyst of the formation of thiolane 1,1-dioxide from thiolene 1,1-dioxides in an alkaline medium at an elevated temperature and pressure is not metallic palladium but its sulfide.

In the presence of palladium sulfide (2.5% $\text{PdS}/\text{Al}_2\text{O}_3$) at an elevated temperature and a high hydrogen pressure, the hydrogenation of 2- and 3-thiolene 1,1-dioxides in a neutral medium and of 3-butoxythiolane 1,1-dioxide in an alkaline solution proceeds at the same rate as in the case where metallic palladium is employed as the catalyst (Table 11). In the hydrogenation of 3-thiolene 1,1-dioxide in an alcoholic alkaline solution on the 2.5% $\text{PdS}/\text{Al}_2\text{O}_3$ catalyst, the same behaviour is observed as in the hydrogenation of 2-thiolene 1,1-dioxide in a neutral medium.^{22, 128} The rate of reaction is proportional to the substrate concentration and the hydrogen pressure. With increase in temperature from 80 to 110 °C, the yield of thiolane 1,1-dioxide obtained from 3-thiolene 1,1-dioxide on palladium sulfide in an alkaline medium initially increases from 78% to 90% ($P = 5\text{ MPa}$, $c = 0.04\text{ M}$, $[\text{KOH}] = 0.45\text{ M}$, $g_{\text{cat}} = 25\text{ g litre}^{-1}$), but then falls to 58% at 135 °C and 22% at 200 °C. In the presence of $\text{Pd}/\text{Al}_2\text{O}_3$, the dependences of the rates of hydrogenation of 3-thiolene 1,1-

dioxide and 3-butoxythiolane 1,1-dioxide on the concentration of alkali in the alcoholic solution are the same: the rate of reaction is proportional to the concentration of alkali raised to the power 0.5.^{22, 125}

The similarity of the kinetics and of the rates of hydrogenation of 2- and 3-thiolene 1,1-dioxides and of 3-alkoxythiolane 1,1-dioxide in an alcoholic alkaline medium at an elevated temperature in the presence of Pd and PdS is a consequence of the similarity of the reaction mechanisms on catalysts of identical composition formed under the influence of the reaction medium. Thiolane 1,1-dioxide is formed from 3-thiolene 1,1-dioxide *via* stages involving its isomerisation to 2-thiolene 1,1-dioxide, the addition of the alcohol with formation of 3-alkoxythiolane 1,1-dioxide, and the reduction of the latter by hydrogen. The low activity of metallic palladium under the given conditions is due to the change in the nature of the active component — the conversion of Pd into PdS .

Thus the hydrogenation of 3-thiolene 1,1-dioxide on palladium-containing catalysts in the presence of added alkali has no advantage over the hydrogenation in a neutral medium on metallic palladium.

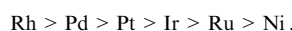
Metallic palladium catalysts deactivated in the hydrogenation of 3-thiolene 1,1-dioxide cannot be regenerated by washing them with solvents (water, alcohol, and acetone), by oxidation with hydrogen peroxide, or by exposure to a stream of nitrogen at 200–300 °C for 10 h. Treatment with hydrogen at 300 °C partially restores the activity of palladium (to the extent of $\sim 80\%$), but full regeneration occurs only after additional treatment with air.¹¹⁵

The XPA spectra of palladium-containing specimens treated with air for 10 h at 100–400 °C exhibit only lines characteristic of metallic palladium (2.23, 1.94, 1.371, and 1.170 Å). In the specimens treated with air at 500 °C, the above lines vanish and those of PdO appear (3.046, 2.667, 2.664, and 2.153 Å).⁸² For the activity of the catalyst, this is unimportant because palladium oxide is readily reduced to the metal even at 20 °C. The thermal stability of palladium compounds is low¹²⁹ and they are therefore relatively easily removed from the surface of the deactivated catalyst. On heating in air, the compounds weakly bound to palladium are desorbed, liberating part of the catalytically active surface. The substances strongly bound to the catalyst, for example a thiol and thiolane, may be oxidised to compounds which have a low toxicity or are nontoxic. Palladium sulfide, formed on interaction of palladium with hydrogen sulfide, is oxidised with evolution of sulfur dioxide, which reacts with palladium in an oxidising medium, affording a surface palladium sulfate. Palladium sulfide and sulfate, deposited on $\gamma\text{-Al}_2\text{O}_3$, are completely inactive in the hydrogenation of 3-thiolene 1,1-dioxide at 20 °C and $P = 5\text{ MPa}$. The activity of $\text{PdS}/\text{Al}_2\text{O}_3$ treated with hydrogen at 300 °C for 20 h is low, but after additional oxidation with air at 200–300 °C for 2 h the catalyst acquires the same activity as metallic palladium deposited on $\gamma\text{-Al}_2\text{O}_3$. A similar treatment of a $\text{PdSO}_4/\text{Al}_2\text{O}_3$ specimen proved ineffective. One cannot rule out the possibility, however, that the surface compounds formed on deactivation of palladium decompose more readily than the bulk-phase PdS and PdSO_4 . Sulfur dioxide, water, and carbon dioxide are evolved on oxidative regeneration of palladium catalysts. They are formed on oxidation of the products of the decomposition of 3-thiolene 1,1-dioxide accumulated on the surface and also as a result of the conversion of the sulfided palladium and not as a result of the oxidation of adsorbed 3-thiolene 1,1-dioxide, alcohol, or thiolane 1,1-dioxide. In the oxidative regeneration of the deactivated $\text{Pd}/\text{Al}_2\text{O}_3$ catalyst, 5–7 times more sulfur and carbon dioxides are evolved than on treating with air a specimen wetted with a 10% solution of the substrate in a mixture of isopropyl alcohol and thiolane 1,1-dioxide. It has been established that the hydrogenation–regeneration cycles involving aluminopalladium catalysts can be repeated many times and that this does not alter the initial activity and duration of the interregeneration period.⁸⁸

VI. Conclusion

As shown above, thiolane 1,1-dioxide can be synthesised by hydrogenating 2- and 3-thiolene 1,1-dioxides in the presence of various catalysts — metals, their complexes, and their sulfides. Group VIII metals have been investigated in greatest detail in this respect. The catalysts based on them exhibit a high activity and make it possible to obtain thiolane 1,1-dioxide in 100% yield by hydrogenation under mild conditions.

The most correct data on the relative activities and stabilities of the metals are obtained when thiolene 1,1-dioxides are hydrogenated in the absence of the distorting influence of mass-transfer processes and in estimating the catalytic properties account is taken of the specific surface of the active component. In terms of their activities in the hydrogenation of 3-thiolene 1,1-dioxide, the massive metals can be arranged in the sequence⁴²



The activities of iridium, ruthenium, and nickel per gram of the metal are approximately the same. Platinum is 6.5 times more active than the above metals and palladium and rhodium are 70 and 280 times more active respectively. When the activities are calculated per m² of the metal surface, the difference is more significant: nickel is the least active; the activities of ruthenium, iridium, and platinum exceed that of nickel by 1–2 orders of magnitude, and rhodium and palladium are more active by 3 orders of magnitude (Table 12). The activity series presented for the metals is close to the series established in the hydrogenation of other unsaturated compounds, for example cinnamic acid.³⁹ In all the hydrogenation reactions, a correlation is observed between the activities of the metals and their properties such as the criterion indicating the extent to which the *d* shell is unfilled, the electron work function, the energy of the bond between hydrogen and the metal, the heat of sublimation, and the crystal lattice parameters. This is explained by the fact that the electronic structure affects the hydrogenating activity of the metal.

The mechanisms of the hydrogenation of 3-thiolene 1,1-dioxide on various Group VIII metals are similar, so that identical kinetics are observed. At a constant 3-thiolene 1,1-dioxide concentration, the rate of hydrogenation is proportional to the hydrogen pressure at *P* up to 2 MPa and, when the latter is increased further, the rate remains unchanged. At a constant hydrogen pressure, the rate of reaction is proportional to the concentration of 3-thiolene 1,1-dioxide up to *c* > 0.1 M, remaining constant at *c* ≈ 0.1 M. The transition from the first to the zero reaction order is associated with the change in the rate-limiting stage as a function of the degree of surface coverage of the catalyst by the reactants, which depends in its turn on the hydrogenation conditions.

Table 12. Comparison of the activities and resistances to sulfur of Group VIII metals in the hydrogenation of 3-thiolene 1,1-dioxide in isopropyl alcohol to which 10% of thiolane 1,1-dioxide has been added at 20 °C, *P* = 5 MPa, and *c* = 0.4 M (according to the data of Mashkina *et al.*⁴²).

Metal	Activity ^a /mol h ⁻¹ g ⁻¹	Specific stability ^b /mmol g ⁻¹	Specific catalytic stability ^b /mmol g ⁻¹	
			in the pres- ence of SO ₂	in the pres- ence of H ₂ S
Rh	1836 (306)	1330 (225)	0.14 (0.023)	0.78 (0.13)
Pd	466 (92)	423 (83)	0.10 (0.020)	0.26 (0.05)
Pt	42 (19)	44 (20)	0.08 (0.035)	0.20 (0.09)
Ir	8 (2)	28 (7)	—	—
Ru	8 (1)	24 (3)	0.07 (0.009)	0.10 (0.012)
Ni	7 (0.1)	140 (2)	1.70 (0.025)	0.15 (0.002)

^a The activity calculated per m² of the metal (mol h⁻¹ m⁻²) is given in brackets. ^b The stability of the catalyst calculated per m² of the metal (mmol m⁻²) is given in brackets.

Group VIII metals are all sensitive to the addition of substances competing with the reactants for adsorption on the catalyst: complete deactivation occurs when less than 0.14 mmol of SO₂ or H₂S per m² of the metal is introduced into the solution (Table 12). In terms of the specific stability in the hydrogenation of 3-thiolene 1,1-dioxide, determined from the amount of thiolane 1,1-dioxide formed on 1 m² of the metal up to the complete deactivation of the catalyst, the Group VIII metals can be arranged in the same sequence as that based on the specific catalytic activity. Thus, the more active the metal the greater its stability (Table 12). A similar behaviour has been found also for supported catalysts: the factors ensuring an increase in activity promote also an increase in the resistance to sulfur. The causes of the existence of a direct relation between the activities and stabilities of the catalysts have been explained in a number of studies.^{22, 93, 100} The stability of the catalyst (*Y*) depends on the ratio of the rates of hydrogenation of 3-thiolene 1,1-dioxide (*W_h*) and deactivation of the specimen (*W_d*). The latter is associated with the amount of poison present in the substrate (*c_p*), the rate of formation of the poison (*W_p*), and the rate of its adsorption (*W_{ads}*).

$$Y = \frac{W_h}{W_d} = \frac{W_h}{c_p W_p W_{ads}}.$$

The content of sulfur dioxide in solution is determined mainly by the purity of 3-thiolene 1,1-dioxide and the reaction temperature but not the nature of the catalyst. For the same degree of purification of the substrate and for the reaction carried out under relatively low-temperature conditions, the concentrations *c_p* are approximately the same. The rates *W_p* on different metals are also similar. The rates of adsorption of SO₂ on catalysts containing 1 mass %–8 mass % of palladium on γ-Al₂O₃, SiO₂, AlSi, or charcoal, calculated per m² of palladium, are of the same order of magnitude (0.4–0.8 mg h⁻¹). Therefore the more active the catalyst in the hydrogenation of 3-thiolene 1,1-dioxide the more stable its operation in this process.

Complexes of Group VIII metals have specific activities in the reactions considered which are not inferior to those of the metals themselves or are actually superior to them. In many instances the binding of the metal in a complex increases the resistance of the catalyst to sulfur. For example, the heterogenised palladium complexes are 3–50 times more stable and the homogeneous platinum complex is an order of magnitude more stable than the corresponding metals.^{32, 35} However, the poisoning of the complexes by compounds of divalent and tetravalent sulfur cannot as yet be fully prevented. In the hydrogenation of 3-thiolene 1,1-dioxide, the complexes undergo a change in their initial structure or are fully decomposed. The possibility of their regeneration has not been investigated, but one may predict the appearance of a number of difficulties in the application of such a procedure.

Transition metal sulfides accelerate the hydrogenation of 2- and 3-thiolene 1,1-dioxides at an elevated temperature and pressure. Rhodium and palladium sulfides exhibit, like the metals themselves, a much higher activity than nickel sulfide; rhenium hemisulfide (Re₂S₇) also exhibits a high activity. However, the specific activities of all the metal sulfides investigated are lower by 2–3 orders of magnitude than those of Group VIII metals. Their advantage consists in the lack of sensitivity to sulfur compounds. However, the stability of the sulfides in the real reaction involving the hydrogenation of thiolene 1,1-dioxides has been very little investigated and one cannot rule out the possibility that the metal sulfides, exhibiting an activity under relatively severe conditions, will also be deactivated by the ring cleavage products condensing on the surface in the form of polymeric deposits. There is virtually no information about the regeneration of such deactivated catalysts.

The catalysts are more stable in the hydrogenation of 2-thiolene 1,1-dioxide. However, this substrate is less readily available than 3-thiolene 1,1-dioxide, from which it is obtained by its

isomerisation. This reaction is reversible and the content of 2-thiolene 1,1-dioxide in the equilibrium mixture is 50% – 60% and, when the product is isolated from the mixture by heating, 3-thiolene 1,1-dioxide decomposes fully. In the hydrogenation of 2-thiolene 1,1-dioxide, the yield of thiolane 1,1-dioxide relative to the more readily available 3-thiolene 1,1-dioxide does not exceed 60%. More rational ways of synthesising 2-thiolene 1,1-dioxide have not so far been found and it still remains more useful to obtain thiolane 1,1-dioxide by hydrogenating 3-thiolene 1,1-dioxide.

In practice, it is preferable to use Group VIII metals, which exhibit a high activity under mild conditions, as catalysts for the hydrogenation of 3-thiolene 1,1-dioxide. Rhodium is more active and stable than palladium, but the latter is less scarce, is cheaper, and is more readily regenerated. It is useful to employ catalysts on a carrier, since the supported metal is more highly dispersed and the catalyst itself exhibits an enhanced thermal stability. In terms of activity per unit surface, palladium is superior by 2–3 orders of magnitude to nickel. However, when a supported nickel catalyst with a high metal content, for example 50 mass % of Ni on Cr₂O₃ or SiO₂ or Raney nickel, is used, it is possible to attain a relatively high productivity and stability per unit mass of the catalyst. A serious disadvantage of nickel catalysts is their high sensitivity to sulfur-containing poisons and the lack of readily available regeneration methods.

As a result of systematic studies at the Institute of Catalysis of the Siberian Division of the Russian Academy of Sciences, catalysts have been proposed for the hydrogenation of 3-thiolene 1,1-dioxide to thiolane 1,1-dioxide — the industrial nickel–chromium catalyst and the palladium-containing IK-71-1 catalyst — and the optimum process conditions have been determined.^{64, 69, 75}

The process is carried out on scaled up apparatus at a temperature below 25 °C and a pressure of 2–5 MPa. After the yield of thiolane 1,1-dioxide has fallen from 100% to 98% (600 h), the IK-71-1 catalyst is regenerated. High-quality thiolane 1,1-dioxide has been produced in this way on the experimental plant of the Salavat Petrochemical Group.¹³⁰

Metallic catalysts, which are traditionally employed in low-temperature hydrogenation processes, suffer from significant disadvantages, the main one being their high sensitivity to poisoning by sulfur compounds in the synthesis of thiolane 1,1-dioxide. Because of this, the starting material must be thoroughly freed from sulfur, the process must be carried out under rigorously controlled conditions, and the catalyst must be regenerated periodically.

Taking into account the growing need for thiolane 1,1-dioxide, which is finding practical application on an increasing scale, it is necessary to intensify the research on the catalytic liquid-phase hydrogenation of thiolene 1,1-dioxides. The principal aspect of such research involves the creation of sulfur-resistant catalytic systems based on a detailed investigation of the hydrogenation and deactivation mechanisms. In this connection, further study of the properties of metal sulfides, both individual sulfides and sulfides modified by means of certain functional additives, in order to create catalysts with an increased activity in low-temperature hydrogenation processes, is becoming a task of primary importance. Another promising aspect may become the study of the catalytic properties of various metal complexes. One may hope that, by varying the type of metal and the nature of the ligands, it will be possible to create an active and sulfur-resistant catalyst for the hydrogenation of thiolene 1,1-dioxides. Such studies may not only lead to the formation of more effective catalysts for the synthesis of thiolane 1,1-dioxide, but they may also help to develop the theory of catalysis and in particular its inadequately elucidated branch — the catalysis of reactions of organosulfur compounds.

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Polypyrrole: a conducting polymer; its synthesis, properties and applications

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Abstract. The synthesis, properties and applications of polypyrrole (PPy), a representative of conducting polymers, are reviewed. Chemical and electrochemical methods for the preparation of PPy and PPy films and the effect of the reaction conditions on the properties of the polymer produced are discussed. The mechanisms of electrochemical polymerisation of pyrrole are compared. The physicochemical properties of the polymer, its morphology and structure are discussed. The mechanism of charge transfer in PPy is considered within the framework of the model of quasi-equilibrium concentrations of polarons and bipolarons. The methods for modification of the electrochemical performance of PPy are reviewed, in particular, synthesis of PPy from pyrrole derivatives with the appropriate electroactive groups and introduction in the PPy of electroactive dopant anions and the effect of those on the electrochemical performance of PPy films are considered. Examples of the use of PPy are given and the prospects for its application in various areas are discussed. The bibliography includes 254 references.

I. Introduction

Not more than two decades ago, researchers considered exclusively polymeric dielectrics or semiconductors that could be made conductive only by means of dramatic changes in their chemical nature (*e.g.*, by heat causing pyrolysis and partial graphitisation of the polymer). The discovery in 1977 of the high conductivity of doped polyacetylene^{1–4} stimulated studies on the synthesis and study of various conjugated polymers. As a result, an entire class of polymeric conductors was developed. Typical representatives of this class are poly(*p*-phenylene),⁵ polypyrrole,⁶ polythiophene⁷ and its 3-methoxy- derivative,⁸ polyaniline.⁹ The common feature of the structure of conducting polymers is polyconjugation in the π -system of their backbone (for polyaniline, this holds only in the case of doped polymer).

The conducting polymers (also called synthetic metals) are polyconjugated, which possess electronic (conductive, magnetic, optical) properties of metals, while retaining the mechanical properties and processibility of conventional polymers. They acquire high conductivity due to incorporation of a small concentration of dopants into the matrix of the initial polyconjugated polymers having conductivity ranging from 10^{-10} to 10^{-5} S cm⁻¹. The resulting materials have conductivities typical of metals or semiconductors, 1 to 10^5 S cm⁻¹.

The doping is performed by means of chemical or electrochemical oxidation (*p*-doping) or reduction (*n*-doping) of a polymer. As a result, the polymeric chains acquire positive or negative charges, respectively.¹⁰ Electroneutrality of the material as a whole is preserved by incorporation of dopants (counterions) from electrolyte solution into the polymeric matrix. The doping is reversible; as a result of dedoping (removal of dopant), the initial polymer can be obtained with its polymeric structure intact. Regulation of the level of doping provides a possibility to prepare polymers with widely varied electric conductivity, from insulating or semiconducting forms of the polymer in the undoped state to highly conductive ones in the strongly doped state.

The conducting polymers attract attention of researchers and engineers from a variety of fields in science and technology as promising electrode materials for energy storage devices (electrochemical batteries and capacitors), electrocatalysts and biosensors based thereon, photoluminescent and electroluminescent materials, 'artificial muscles', gas separating membranes, anticorrosive coatings, electromagnetic shields, materials for microlithography, electrophotography, *etc.*¹¹ In addition, the possibilities to produce conducting polymers electrochemically and to control their properties by electrochemical means are of interest on their own. To date, a number of reviews and books on conducting polymers have been published. Unfortunately, the topic is not extensively reviewed in the Russian literature. In this paper, we review the properties of polypyrrole (PPy), which is a typical representative of conducting polymers and manifests characteristic features of this class of materials.

II. Methods of polypyrrole preparation

1. Chemical synthesis

Among other conducting polymers, PPy and its derivatives are of particular interest, owing to their high conductivity, stability in the oxidised state and interesting redox properties. The simplicity

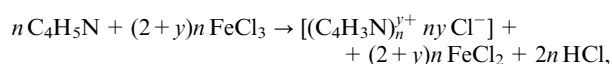
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of the synthetic procedures and availability of the initial monomers are also attractive features of PPy.

Chemical synthesis of PPy has a long history.¹² Polypyrrole prepared by oxidation of the monomer with chemical oxidants has a form of black powder. Aqueous or anhydrous FeCl₃,^{12–15} other salts of iron(III) and copper(II) are widely used as chemical oxidants.^{16–19} The use of halogens and organic electron acceptors as oxidants for PPy synthesis has also been reported.^{20,21} The yield and conductivity of the PPy produced are affected by a variety of factors, among which are the choice of solvent and oxidant, initial pyrrole/oxidant ratio, duration and temperature of the reaction. At the optimal ratio¹³ of Fe(III)/monomer which is 2.4, the yield of PPy approaches 100%. Shorter times of polymerisation and lower temperatures (0 to 5 °C) result in enhanced conductivity of PPy produced.¹⁸ For PPy prepared by monomer oxidation with FeCl₃ in various solvents (water, alcohols, benzene, tetrahydrofuran, chloroform, acetone, acetonitrile (AN), dimethylformamide),¹⁴ the highest conductivity was observed for PPy prepared in methanol solution (190 S cm^{–1}). Controlled variation of the oxidising potential of the reaction medium [it was changed through the ratio of FeCl₃ to FeCl₂ (Ref. 14) and also using a binary AN/methanol solvent²²], provided a possibility to enhance conductivity of PPy to 220 S cm^{–1} in the former case and to 328 S cm^{–1} in the latter. When PPy is produced by oxidation in the presence of FeCl₃, the polymer is doped with Cl[–] anions; the overall reaction can be represented by the following stoichiometric equation^{12,14}



where y is the degree of PPy oxidation (doping level).

In earlier works, the degree of PPy oxidation was determined from the Cl/N ratio using the data from elemental analysis. The Cl/N ratio varied from 0.21 (see Ref. 12) to 0.34 (Refs 13, 14). In Ref. 19, the Cl/N ratio for PPy prepared from aqueous solution was 0.33 and substantially exceeded that for the polymer produced from methanol and AN. X-Ray photoelectron spectroscopy (XPS) revealed that chlorine atoms in the polymer are in three chemical states, namely, ionic, covalently bonded and an intermediate one; the latter is similar to the chloride anions in metal chlorides (including FeCl₃ and FeCl₂). It was noticed¹² that when PPy was treated with solution of FeCl₃ in nitromethane, the iron-containing FeCl₄[–] anions were incorporated in the polymer. Possibly, the intermediate species of chlorine is related to iron chlorides.¹⁹ In spite of the high concentration of incorporated chlorine, only a Cl/N ratio equal to 0.25 corresponded to y (25% of oxidised monomer units). Thus, the elemental analysis is insufficient to determine the true degree of PPy oxidation.

The conductivity and stability of PPy powder produced by means of chemical oxidation were substantially improved. However, formation of PPy films or coatings on another material remained problematic. This problem was partially solved by PPy deposition from gas with FeCl₃ used as an oxidant.^{23–25} This method provided a possibility of producing free film or PPy coatings having high mechanical properties on substrates of any shape. The mechanical performance of PPy powder could also be improved by preparation of composites filled with it, composites with poly(ethylene oxide) in particular.^{23,26,27}

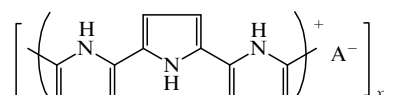
The method of chemical oxidative polymerisation constituted a basis for the layer-by-layer deposition of PPy and polyaniline (PAni).²⁸ The authors of this work report that the polymers have more regular structure and higher crystallinity than those produced electrochemically.

2. Electrochemical synthesis

Electrochemical polymerisation provides a number of advantages over chemical methods. The first is that the reaction product is an electroactive film attached to the electrode surface and having high conductivity. Second is that the yield in charge terms is close to 100%; this provides a possibility of controlling the mass and

thickness of the film. And finally, the properties of the film produced can be controlled directly in the course of preparation. In 1968, Dall'Olio *et al.*²⁹ obtained a PPy film with conductivity of 8 S cm^{–1} by electrolysis of pyrrole solution in the presence of sulfuric acid; the polymer was obtained in the form of powder deposited on the electrode surface. In 1979, Diaz *et al.*^{6,30} prepared the polymer in the form of flexible films with conductivity of 100 S cm^{–1} by electrolysis of an aqueous solution of pyrrole. This work gave a start to the extensive use of electrochemical synthesis of PPy (and other conducting polymers). The PPy films are obtained in doped (conducting) form directly in the course of synthesis; they can be transferred to neutral (insulating) form by means of electrochemical reduction.

Electropolymerisation (EP) of pyrrole (and electrosynthesis of other conducting polymers) differs from other polymerisation reactions, including the radical ones, that are initiated electrochemically.³¹ The anodic oxidation, which results in the formation of conducting polymer, has the stoichiometry of 2.07 to 2.6 F per mole of monomer.^{32,33} Of those, only 2 F mol^{–1} are related to the polymerisation as such and extra charge, to the oxidation (doping) of the polymer film. Since the oxidation potential of the monomer is always markedly higher than that for the polymer, the two processes, the formation of polymer and its oxidation proceed in parallel and are accompanied by the incorporation of counterions into the polymer matrix. The structure of the PPy formed can be represented as³⁴



where A[–] is an anion.

The doping level for PPy (number of anions per monomer unit), depending on the nature of anions and conditions of synthesis, varies within 0.1 to 0.5. Switch-off of the current in the course of PPy electrosynthesis is immediately followed by the arrest of the chain growth; the mass of the polymer film is directly proportional to the charge passed.^{35–37}

Electropolymerisation of pyrrole can be performed in both aqueous and non-aqueous media, such as AN, propylene carbonate (PC), dichloromethane.^{32,38–41} However, with increasing nucleophilicity of solvent, the film growth is inhibited due to the interaction of solvent with the primary products of monomer oxidation. The film does not form in such nucleophilic aprotic solvents as dimethylformamide, dimethyl sulfoxide, hexamethylphosphoramide, unless the nucleophilicity of solvent is reduced by addition of a protic acid.⁴² Apart from that, the side reactions occurring on the film surface can affect EP in these solvents. Thus, a thick PPy film was prepared from a NaClO₄ solution in dimethylformamide.⁴³ An increase in the rate of EP was observed when the temperature decreased. This increase was explained by the relative inhibition of the side reaction of film passivation, which resulted in lower conductivity. The rate of EP grew with increasing concentration of ClO₄[–] anions that act as retardants for the passivating reactions in the electrolyte.

According to the extensively used procedure of Diaz,³⁰ 1% of water is added to AN solution; this results in improved properties of the film (adhesion to electrode, uniformity). The better PPy films were obtained with 2% of water in AN electrolyte.⁴⁴ However, a high content of water in the electrolyte (over 20%) results in deterioration of such film properties as tensile strength and electroconductivity.

The working electrode for electrosynthesis of conducting polymers is usually made of corrosion-resistant materials that are stable at high anodic potential, namely Pt, Au, Pd, Rh, Ir,^{38,39,41} conducting In₂O₃–SnO₂ glasses,^{45–47} carbonaceous materials (graphite, vitreous carbon).^{39,40,48} Syntheses of conducting polymers on Al,^{41,49,50} Ta,^{41,51,52} Fe, Cu, Ti, Ni, Cr, Nb, stainless steel^{41,53} were reported. It was found⁴¹ that the nature of metal substrate virtually does not affect the kinetics of PPy

synthesis. Ta, Ti, Nb, and Al are exceptional; their behaviour is substantially affected by the oxide layer between a metal and PPy. The PPy film was reported to act as a protective coating on a Ta substrate.⁵⁴ Such semiconducting materials as Ge, GaAs,⁵⁵ CdS,^{56,57} CdSe,⁵⁷ doped TiO₂⁵⁸ were also used as electrodes; for these materials EP occurs under additional illumination.

In order to obtain reproducible results, one must carefully prepare the electrode surfaces before synthesis and also use high-purity chemicals.^{39,55} High quality polymer films are usually produced in three-electrode cells with the regions of the working and the auxiliary electrodes separated with a diaphragm. Stirring of the electrolyte solution hinders polymer deposition on both pure and PPy-coated electrodes.^{39,59} Prior to the experiment, the electrolyte solution should be purged with nitrogen or argon in order to remove oxygen, because films prepared in the presence of oxygen have inferior properties.⁶⁰

In conventional EP of pyrrole, the polymer film grows as a coating on the anode immersed in electrolyte solution. When a platinum electrode floating on the surface of electrolyte was used,⁶¹ a uniform thin film that grew along the gas-liquid interface from the electrode to the cell walls was formed. The structure and properties of this film differ from those of PPy films prepared using the conventional method. Supposedly, the polymer has a branched (possibly, three-dimensional network) structure.

Electropolymerisation of pyrrole can be performed in various regimes, in particular, potentiostatic,^{32,62} galvanostatic,^{35,40,63} potentiodynamic^{36,64} and pulsed one.⁶⁵ The mechanical properties of the films, their morphology and electrochemical behaviour depend on the conditions of preparation, including the nature of solvent, pH of the electrolyte, the purity and concentration of the initial monomer, and the nature and concentration of electrolytic salt.^{32,36,42,62,66-68}

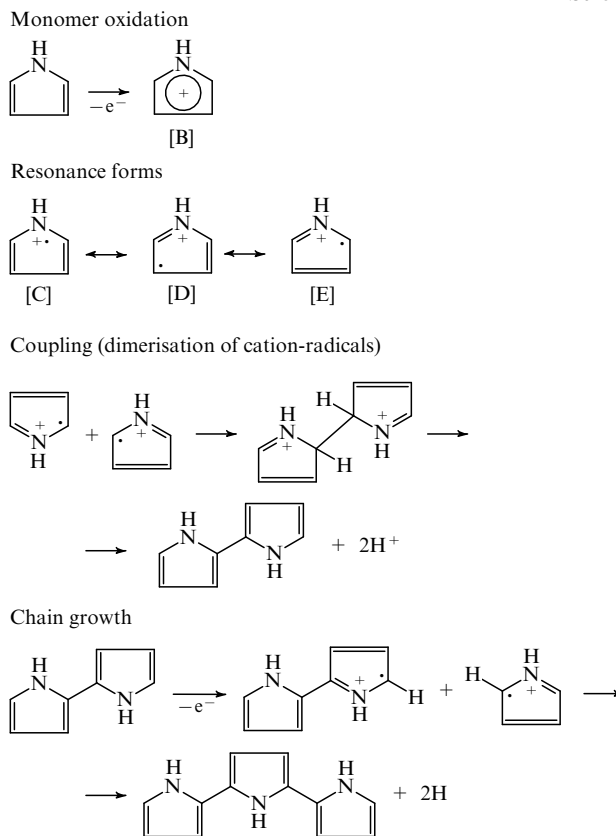
III. The mechanism of electrochemical synthesis of polypyrrole

The oxidation of pyrrole to PPy is irreversible. The mechanism of this reaction was extensively studied;^{33,37-39,41,44,45,59,64,68-81} yet, the problem still remains not fully resolved. Among the mechanisms proposed, two have gained the greatest interest. One of those is the oxidative coupling of monomer molecules (Scheme 1).³⁷ The first stage of the reaction is the electrode oxidation of monomer molecules yielding radical cations with the radical state delocalised over the pyrrole ring (B). The maximum spin density is at the α -position;⁶⁹ hence, of the three possible resonance states, C, D and E, the latter is the most stable. The radical cations dimerise (this is the rate-controlling stage of the reaction^{37,64,81}) and expel two protons. The dimers, owing to stronger conjugation, are more readily oxidised under the given reaction conditions than the monomer. The chain growth proceeds by addition of a newly formed radical cation to an oligomeric one. Some authors deny the possibility of dimerisation of radical cations because the latter experience strong Coulombic repulsion.^{38,39,45}

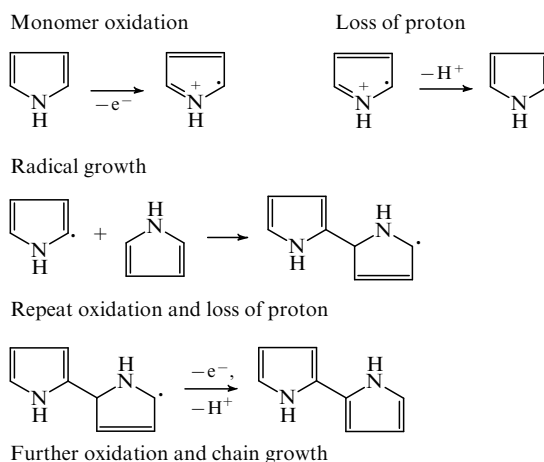
The alternative mechanism proposed for polymerisation of pyrrole is the free radical reaction (Scheme 2).^{38,45} This scheme implies that formation of a radical cation on the anode is followed by the loss of a proton and attack of the radical on a neutral monomer. After reoxidation of the dimeric radical and proton loss, the dimeric molecule can experience subsequent oxidation, which results in chain growth. The release of protons in the course of oxidation of pyrrole was observed experimentally.⁷²

Kinetic studies using isotopically labelled reactants and experiments with radical traps⁷⁰ showed that Scheme 1 is more probable. According to Scheme 2, any free-radical initiator would trigger the polymerisation of pyrrole, which is not the case. In addition to that, Scheme 2 cannot account for the experimentally observed fact that polymerisation proceeds only when monomer oxidation occurs in parallel with the oxidation of the polymer (the

Scheme 1



Scheme 2



oxidation potentials for the dimer and oligomers of pyrrole are lower than that for the monomer).

The pyrrole dimers were detected in the electrolyte.^{71,72} Spectroelectrochemical studies showed⁶⁴ that radical cations and dications of bipyrrrole are the primary species observed at the early stages of electrolysis. Chronoamperometric methods with two-step variation of potential (using ultramicroelectrodes) showed⁷⁷ that EP of pyrrole proceeds according to the mechanism of oxidative coupling and that dimerisation of the radical cations is the rate-controlling stage. The lifetime of the radical cation was estimated⁷⁷ to be $\sim 20 \mu\text{s}$. The experiments using rotating ring-disc electrodes provided an estimate of the rate constant for the formation of the radical cations of pyrrole⁸² within the range 10^7 to $10^8 \text{ litre mol}^{-1} \text{ s}^{-1}$.

The stability of radical cations is an important factor in EP. The radical cations with moderate stability possess the chemical selectivity which favours radical coupling in the film formation. More stable radical cations diffuse away from the surface of the

electrode; this results in the formation of soluble oligomers. The radical cations with lower stability are more reactive and react with solvent or other nucleophiles close to the electrode surface. Therefore, EP of pyrrole in the presence of nucleophilic anions (halides, hydroxides, cyanides, acetates) results in lower yield and smaller molecular mass of the polymer and formation of soluble products.⁸³ The yield of polymer and its conductivity grow with the increasing donor number of the solvent (which reflects the strength of interaction between a solvent and radical cations) in the series nitromethane < nitrobenzene < benzonitrile < AN < PC.⁸⁴ In solvents with large donor numbers (AN, PC), the intermediate radical cations selectively react with the monomer in α -position; this results in formation of polymer with highly regular structure.

It was supposed in the earlier studies^{37,38} that, prior to oxidation, the neutral monomer molecule is adsorbed on the electrode surface. However, further studies using a rotating ring-disc electrode and differential ellipsometry showed that the first stage in polymer deposition is polymerisation in solution and that nucleation of PPy on the electrode surface occurs only after the oligomer chain acquires a certain length at which it becomes insoluble.^{39,74}

The growth mechanism of nuclei of conducting polymers is debated in the literature. In a number of studies,^{38,75,82} the EP is considered as nucleation and growth of the polymer coating analogous to the electrochemical deposition of metals. This analogy is supported by the nucleation loop present in the cyclic voltammograms^{38,74,75} and by the increase in the current on the $I-t$ curve during potentiostatic EP.^{27,38,44,75} The mechanism of these electrochemical phenomena (especially the rising $I-t$ transients) implies an increase in the electroactive surface of the electrode in the course of the process. It was reported^{27,38,76} that addition of a pyrrole monomer to the end of a polymer chain does not bring about an increase in the electroactive polymer surface and implies unidimensional growth of the polymer; under such conditions, dendrites grow in the direction of the electric field on the electrode surface. The experiments on 10- μ m-diameter electrodes⁵⁹ showed that the polymer growth resulting in the nuclei expansion occurs primarily due to deposition of oligomeric species on top of the existing nuclei rather than due to monomer addition to a polymer chain. Here, similar to electrochemical deposition of metals, the pyrrole and its oligomers from solution are preferentially oxidised on the polymer surface rather than on the electrode.

There are two regions in the Tafel plot of the synthesis current versus potential.^{45,78} The inflection in the $\lg I-E$ curve indicates that the reaction mechanism gradually changes with the changing nature of the electrode surface. In the first region, the oxidation of pyrrole results in the polymer nucleation on platinum (the reaction order with respect to pyrrole is unity). When the electrode is covered with a polymer film, both the slope of the curve and reaction order with respect to pyrrole (equal to 0.5) change; the film growth is controlled by the electrochemical reaction on the polymer. The reaction order in the second region coincides with that measured using coulometry and microgravimetry *ex situ*.^{64,79} The earlier electrochemical studies that considered the initial stages of electrochemical synthesis reported the pyrrole oxidation to be first order on a platinum electrode.^{39,41,80} The reaction order of 0.5 with respect to pyrrole (at greater conversions) may indicate that the growth of polymer is fractal in its geometry.⁸⁵

The rate of EP and yield of the polymer are substantially enhanced by addition of 2,2'-bipyrrole in the electrolyte in the course of the PPy synthesis.⁸⁶ The addition of 2,2'-bipyrrole also shortens the delay time associated with the stage of dimerisation of radical cations.

An increase in the rate of pyrrole EP is also observed with a trace of water in AN electrolyte;^{68,81} this is related to reduced Coulombic repulsion of two hydrated radical cations of pyrrole. Addition of bromide anions to the electrolyte causes electrocatalytic promotion of pyrrole EP.⁶⁸ The electropolymerisation

is also markedly accelerated in the presence of small amounts of iron(III) and copper(II) chlorides.⁸⁷

In potentiodynamic regime, EP from aqueous solutions starts at lower potentials than in AN (0.35 V compared with 0.65 V *vs.* Ag/AgCl).^{36,88} In aqueous solutions, the film grows faster than in AN (the increment of the mass in each cycle is higher). The measurements of anodic charge related to EP suggested that the film grew proportionally to the number of cycles. Use of electrochemical quartz microbalance showed that in both electrolytes the PPy films grow nonlinearly at the initial stage of EP and constant-rate growth is attained further.⁸⁸

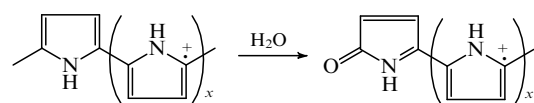
The rate of EP depends on the nature of the anions in electrolyte.^{41,62,88} For example, the PP/poly(styrenesulfonate) film grows much faster than the PPy/Cl⁻ film. It is supposed⁶² that larger anions are more strongly adsorbed on the electrode surface and this promotes the first stage of EP. Table 1 summarises the parameters of EP of pyrrole in the presence of various electrolytes.⁶²

Table 1. Effect of the nature of organic anion on the rate of pyrrole EP and the properties of the film.⁶²

Electrolyte anion	Conductivity /S cm ⁻¹	Growth rate /nm s ⁻¹	Yield of PPy /cm ³ mQ ⁻¹
Dodecyl sulfate	15.3	25.6	1.3
Toluene sulfonate	9.8	20.1	1.0
Dodecylbenzene sulfonate	4.7	23.8	1.2
Poly(<i>p</i> -styrene-sulfonate)	7.3	7.9	0.4

A mechanism of electrochemical synthesis of PPy from aqueous solutions is proposed;⁴¹ according to this mechanism, the EP involves a complex of pyrrole with anion and proton. The existence of such a complex was confirmed by means of IR spectroscopy. It was supposed⁸⁹ that protonated pyrrole is the active species.

EP of pyrrole, in the presence of water, in addition to the above-described dimerisation of the pyrrole cation radicals (see Scheme 1), can involve the side reaction of the cation radicals with water yielding undesirable electrochemically inert products.^{90,91}



This polymer formed thus has shorter chains and, hence, poorer mechanical and electronic properties compared with PPy prepared from AN solution.

IV. Physical and mechanical properties of polypyrrole

PPy films thinner than 1 μ m have different spectral properties depending on the conditions of synthesis and degree of PPy oxidation; with the increasing degree, the colour of the films changes from yellow to the blue and, ultimately, black.^{32,92} The films have good adhesion to the substrate but at a thickness of over 10 μ m are relatively easily peeled off the electrode.^{34,93} The adhesion depends on a number of factors including the nature, coarseness, hydrophobicity of the electrode surface and the solvent used.^{39,53,94}

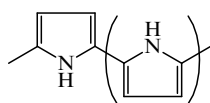
The stability in air of the doped PPy films is relatively high; their degradation occurs only above 150–300 °C (depending on the dopant anion).^{6,34,93,95,96} Thermal degradation of PPy starts with the loss or decomposition of dopant.⁹⁷ Further deprotonation (or further dopant loss) at higher temperatures is always

accompanied by formation of imine-like structures in the polymer. The thermal stability of the films obtained by means of EP improves after their treatment with H_2SO_4 , Na_2SO_4 or NaHSO_4 ; upon such treatment, no morphological changes are observed in the polymer.⁹⁸ The films of reduced (insulating) PPy are relatively stable when stored under an inert atmosphere and unstable in air; initially transparent and yellow, they rapidly turn dark, their conductivity increases to 0.01 S cm^{-1} and the films irreversibly lose their ability to undergo redox transition.^{32, 94, 99}

The films prepared by electrodeposition in the presence of inorganic anions are relatively brittle; their mechanical properties are usually higher than those of the films doped with bulky organic anions.^{42, 66, 100} The tensile strength for PPy films with different dopant anions varies from 8 to 100 MPa; the elongation at break, is within 2%–8%; the Young's modulus, 0.4–4 GPa.^{42, 100, 101} The elongation at break can be substantially enhanced (to 70%), when PPy is synthesised at low temperatures.¹⁰¹ According to Ref. 102, the elasticity of the freshly prepared films, which contain solvent, is higher, their elongation at break reaches 60%. The films reversibly absorb solvent (water, AN); they also absorb water vapour from air.^{35, 103}

Studies by means of scanning and transparency electron microscopy showed that PPy films are compact and have no voids.^{6, 32, 67} The apparent surface of the PPy-coated electrode measured using impedance spectroscopy and small-angle neutron scattering is 40–50 times higher than the area of underlying platinum electrode, according to scanning electron microscopy it is 2.2 times higher.¹⁰⁴ The latter method does not provide a possibility to assess microporosity of the polymer. The microstructure and porosity of the polymer depend on the dimensions of the dopant anion.¹⁰⁵ Thus,¹⁰⁶ the density of $\text{PPy}/\text{ClO}_4^-$ films is 1.52 and that of $\text{PPy}/\text{toluenesulfonate}$, 1.37 g cm^{-3} . The films prepared from aqueous solutions are more porous and have lower density than those synthesised in AN.^{36, 107} In microphotographs, the surface of PPy films prepared in aqueous solutions looks like a cauliflower.^{32, 35} The films synthesised in non-aqueous media and those with large organic anions have a smoother-looking surface.^{36, 62, 107, 108}

Polypyrrole is amorphous and usually gives only a diffuse halo in X-ray diffraction patterns.^{6, 101} The electron diffraction showed that there are up to 15% (of total volume) of crystalline domains in the bulk of amorphous PPy.⁶⁶ The experimental data indicate that the crystalline regions have a monoclinic lattice; the pyrrole rings are oriented so that nitrogens of neighbouring rings are oriented in opposite directions.



The data from IR spectroscopy,¹⁰⁹ NMR,^{109, 110} analysis of the products of oxidative decomposition of PPy¹¹¹ indicate that pyrrole rings couple at α – α' -positions. This inference is confirmed by the fact that α -substituted pyrrole derivatives do not polymerise upon oxidation.⁴² The calculations show that a certain number of bonds are formed at the β -position.⁹⁵ Electropolymerisation of 3-methyl- and 3,4-dimethyl-substituted monomer yields a polymer with a more regular structure and higher conductivity because for these monomers coupling at the β -position is blocked.¹¹²

The PPy chains are planar and are arranged in layers parallel with respect to the film surface; the interplane distance is 0.341 nm.¹¹³ Alkyl substituents in PPy do not affect the planar arrangement of the chains.¹¹⁴ The PPy chains within the planes are not oriented. The dopant anions intercalate the interplane spaces between the PPy chains.¹¹⁵ X-Ray photoelectron spectroscopy showed that¹¹⁶ electrostatic interactions between the oxidised PPy chains and dopant anions (ClO_4^- , polyvinylsulfonate) occur *via* the π -system of the rings rather than *via* heteroatoms of the rings. The sandwich structure is also formed in the case of PPy doped with alkylsulfate and arenesulfonate anions.¹¹⁷ PF_6^- anions pre-

serve their structure in the polymer matrix of PPy,¹¹⁸ whereas FeCl_4^- anions experience strong distortion of their tetrahedral structure due to the formation of hydrogen bonds.^{119, 120} There are also indications that there is a strong interaction between charged PPy chains and dodecylsulfate anions.¹²¹

The data of electron diffraction indicate that polymer chains are ordered.¹²² Studies of conductivity, which is related to both fast charge transfer along the polymer chains and rapid exchange between the macromolecules, also indicate that polymer chains are to some extent ordered.¹⁰⁹ The degree of polymer ordering strongly affects its conductivity.¹²³ X-Ray diffraction showed that PPy films prepared in the presence of multicharged anions are more regular than those with single-charged anions.¹¹⁹

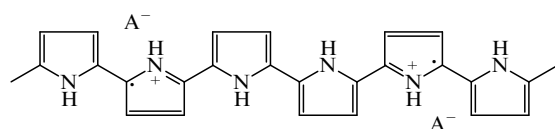
Numerous studies of the chemical structure of PPy indicate that its elemental composition fits the formula $\text{C}_4\text{H}_3\text{NA}_{0.3}$, where A is the anion in the presence of which electrosynthesis was performed.^{6, 32, 34, 93} The percentage of carbon and hydrogen in the polymer often exceeds the theoretical values, sometimes oxygen is also present. The actual cause of these deviations is not unambiguously understood; it was however found that the polymer contains water or another solvent,^{35, 103} and that PPy chemically reacts with the atmospheric oxygen.^{6, 32, 40, 94} Polypyrrole is insoluble in organic solvents and this makes measurements of its molecular mass a difficult problem.

V. The nature of electronic conduction of polypyrrole

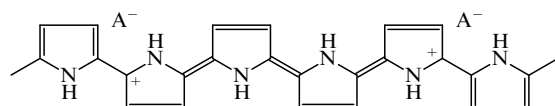
The interest in the electronic properties of polyconjugated polymers was boosted by the 1964 paper by Little,¹²⁴ where the possibility of superconductivity in unidimensional structures was predicted.

The neutral (undoped) PPy is a dielectric with the gap of 4 eV.¹²⁵ Upon oxidation (doping), the π -electrons are removed from the upper level of the valence zone with a simultaneous shift of the boundary π -levels (the highest occupied and the lowest vacant) to lower energies. The gap reduces to $\leq 2.5 \text{ eV}$ and the polymer becomes a semiconductor.

Of special interest in PPy conduction is the mechanism of charge transfer. The charge carriers are the polarons and bipolarons formed upon doping.^{126, 127} In chemical terms, the formation of a polaron is equivalent to formation of a radical cation



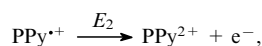
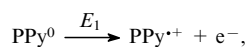
and of a bipolaron, to dication



The polaron and bipolaron in PPy are extended structures spread over three to four monomeric units of the chain.¹²⁸

The separation of the positive charge on the chain in the bipolaron structure predetermines the energy of the system. The further the positive charges are apart the lower the stability of the system, since it contains more rather unstable quinoid rings. The calculations of the energetics showed that formation of a bipolaron requires 0.45 eV less than formation of two polarons.^{126, 127} This result led to a suggestion that bipolaron is the major charge carrier in PPy.^{129, 130} This suggestion was to a certain extent confirmed experimentally by the studies of optical absorption spectra^{131, 132} and ESR.^{133, 134} The ESR spectroscopy is extensively used for studies of doping in PPy, because it provides a possibility to measure the concentration of spins associated with polarons ($S = \pm 1/2$). Bipolarons that are spinless ($S = 0$) are not detectable by means of ESR. The authors of Ref. 134 claim that

only spinless charge carriers are present in the polymer because there is no correlation between the conductivity and concentration of spins in the polymer. The experimental data of Refs 135 and 136 were interpreted in terms of quasi-equilibrium concentrations of polarons and bipolarons formed in the two-step redox process:



where E_1 and E_2 are the quasi-standard potentials of formation for polarons ($\text{PPy}^{\bullet+}$) and bipolarons (PPy^{2+}).

The data of Refs 135 and 136 agree well with the measurements of PPy conductivity as dependent on the partial charge per monomer unit.¹³⁷ The strong correlation between the enhanced PPy conductivity and concentration of polarons is illustrated by Fig. 1. When the conductivity reaches the plateau, the concentration of polarons decreases; this decrease can be attributed to the formation of bipolarons. The obvious relation of the conductivity to concentration of polarons at low doping levels disproved the previous hypothesis^{133,134} that conduction in PPy is solely spinless. The spectroelectrochemical measurements showed¹³⁸ that polarons in PPy and PANi are stable species and their maximum concentrations in respective polymer are 80% and 90% at 50% of the reversible charge. Further investigation of PPy by means of *in situ* impedimetry¹³⁹ showed that polarons and bipolarons equally contribute to conductivity, being charge carriers with the same mobility. Further,¹⁴⁰ it was inferred that in PPy the polaron and bipolaron are partners and electron hopping is easier between a polaron and bipolaron than it is between a neutral chain fragment and polaron; this is due to the fact that in the former case planarity of the states is similar and this reduces the conformational activation energy. Similar results were obtained for PANi.¹⁴¹

The concentrations of polarons and bipolarons in PPy in the

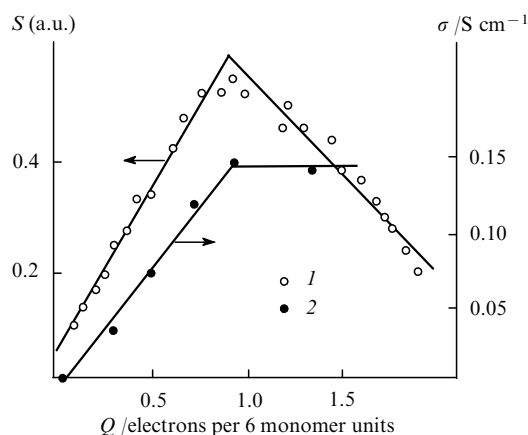


Figure 1. The dependences of (1) spin concentration¹³⁵ and (2) conductivity¹³⁷ on the oxidation charge (Q).

course of oxidation and reduction were studied using ESR spectroscopy and laser electroreflectance.¹⁴² The equilibrium concentration of polarons in PPy increases with potential growing from 0 to 200 mV and reduces for $E > 200$ mV, owing to the formation of bipolarons.

The conducting polymers are quasi-unidimensional conductors rather than unidimensional. Of particular interest are interchain interactions and charge transfer. It was noted¹⁴³ that dopant not only compensates the charge of the free charge carriers but also enhances the probability of interchain charge transfer due to a strong overlap of the atomic orbitals of the dopant with the π -orbitals of the carbon atoms. Since the polymer chains are oriented mainly parallel to the film surface, the conductivity along the surface ($s_{\parallel}$) is usually higher than that perpendicular

($s_{\perp}$). In the former case, conductivity involves less interchain charge hops. The anisotropy of conductivity ($s_{\parallel}/s_{\perp}$) amounts to 360.¹⁴⁴

The most regular alignment of the macromolecules (more ordered structure) and, therefore, higher conductivity of the films is achieved when the synthesis is performed at low temperatures.^{100,101,112} The conductivity of PPy films prepared in PC solution at -20°C is 300 S cm^{-1} and for $+20^{\circ}\text{C}$ it is 97 S cm^{-1} .¹⁰¹ Due to the alignment of the polymer chains the highest conductivity achieved for PPy, 3000 S cm^{-1} , was attained under conditions of low-temperature electrosynthesis.¹⁴⁵

The temperature dependence of the conductivity fits the equation

$$\lg \sigma = A + BT^{-1/(n+1)},$$

where $n = 1, 2, 3$.

Such a dependence is typical of the hopping mechanism of conduction with a variable hop length.¹⁴⁶ With decreasing temperature, the conductivity drops (which is characteristic of semiconductors). However, there are also reports (cf.¹⁴⁷) that the conductivity increases with decreasing temperature (such behaviour is inherent in metals).

The conductivity of the polymers strongly varies depending on the conditions of their synthesis. Major changes in the conductivity usually occur at the earlier stages of doping, its further increase is insignificant.^{100,148}

The conductivity of PPy films varies by several decimal orders depending on the nature of an anion introduced into it during synthesis (Table 2). A change in the nature of solvent changes the order of anions in the series of conductivities. Usually, the PPy films prepared in AN electrolytes are more conductive than those synthesised in aqueous solutions. This is due to a larger conjugation length of the polymer and better contact with the metal electrode in the former case.³⁶ The electrical conductivity is, in the majority of cases, higher for anions with lower nucleophilicity.¹⁴⁹ Electrosynthesis of PPy in aqueous solutions in the presence of bulky organic anions (toluenesulfonate, dodecylbenzenesulfonate, dodecylsulfate) results in enhanced quality and conductivity of the films produced, compared with those of the PPy/Cl^- and $\text{PPy}/\text{ClO}_4^-$ films (see Refs 62, 108, 149).

At the same time, the exchange of a counterion in as-grown

Table 2. Conductivity of PPy films synthesised from aqueous electrolytes and from AN.^{42,93,149}

Dopant anion	Conductivity (S cm^{-1})	
	aqueous solution	AN
BF_4^- (fluoroborate)	2–2.5	30–100
ClO_4^- (perchlorate)	5–6.5	60–200
AsF_6^- (hexafluoroarsenate)	2.4–2.8	30–100
HSO_4^- (hydrosulfate)	3.5	0.3
CF_3SO_3^- (triflate)	3.4	0.3–1.0
CF_3COO^- (trifluoroacetate)	1.0–1.3	12
$p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3^-$ (tosylate)	89–121	20–105

PPy for other anions from electrolyte but slightly affects the conductivity of PPy; the replacement of an anion changes the structure of the polymer matrix, yet not to the extent that it will change the barrier height and hopping frequency.^{40,150} On the other hand, for the films being prepared with a particular anion, the structure of the forming polymer matrix substantially depends on the nature of dopant and, therefore, the conductivity is strongly affected by the nature of an anion.

The effect of pH of electrolyte on conductivity of PPy films synthesised therein was extensively studied^{38,62,117,149} (Fig. 2). In alkaline media, thin insulating films are formed.³⁸ The conductivity goes through a maximum at the synthesis potential of 0.6 V (vs. saturated calomel electrode) in aqueous solution¹⁰⁰ (Fig. 3), the

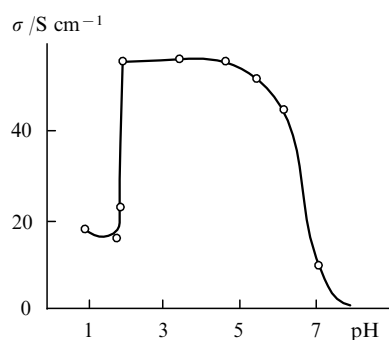


Figure 2. The dependence of PPy conductivity on pH of the electrolyte.¹¹⁷

corresponding maximum is observed in the dependence of conductivity on the current density.^{117, 151} Electrosynthesis of PPy films at current densities over 5 mA cm^{-2} results in reduced conductivity of the films with both organic and inorganic dopant anions.¹⁰⁸

The structure of PPy films doped with ClO_4^- , BF_4^- and,

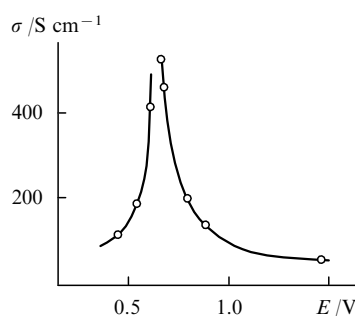


Figure 3. The dependence of conductivity of PPy films on oxidation potential (vs. saturated calomel electrode); synthesis from aqueous solution of 0.25 M pyrrole + 0.8 M sodium tosylate.¹⁰⁰

correspondingly, their conductivity depend on the nature of solvent (due to above-described causes). The films doped with strongly basic anions (high pK_a)⁸⁴ do not show such a dependence (Fig. 4).

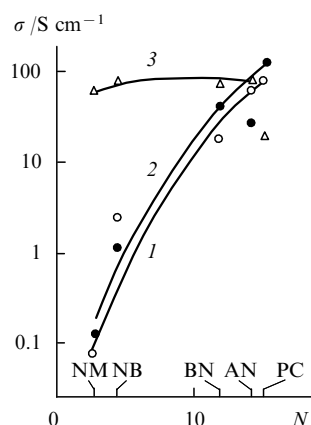
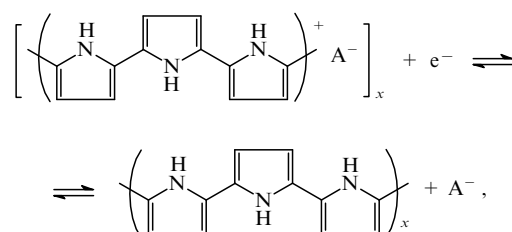


Figure 4. The dependence of conductivity (σ) of PPy films prepared in the presence of ClO_4^- (1), BF_4^- (2), tosylate anion (3) on the donor number of solvents (N):⁸⁴ nitromethane (NM), nitrobenzene (NB), benzonitrile (BN), acetonitrile (AN), propylene carbonate (PC).

When conducting PPy films are stored in air, their conductivity decreases.¹⁵¹ The conductivity of the films with bulky organic anions reduces much more slowly. Thus, the electrical properties of PPy/dodecylbenzenesulfonate do not change after a 6-month storage in air.¹⁴⁹

VI. Electrochemical properties of polypyrrole

The very first electrochemical studies showed that PPy is sufficiently stable and can be used as a non-metallic electrode material.^{30, 93, 152} Its intrinsic redox reaction associated with doping and dedoping must be taken into account as was first shown by Diaz *et al.*^{32, 93, 153} in 1980. The following equation for this reaction was proposed on the basis of electron balance and elemental composition.



where A^- is the anion.

The positive charge of oxidised segments in PPy chains is counterbalanced by the anions of electrolyte that are incorporated in the polymer; the anions leave the polymer matrix and return to the solution when PPy is reduced. The method of cyclic voltammetry (CVA) is extensively used in studies of redox processes in conducting polymers. In this method, the potential is linearly scanned up to a certain preset limit and then is reversed to the initial value.^{32, 38, 88, 91, 107, 154–158} Figure 5 shows a typical voltammogram (VA) of a PPy film. The anodic peak in VA is related to the oxidation of PPy, the cathodic one, to its reduction to the neutral form according to the above equation. The maxima of the peaks in VA correspond to the maximum polaron concentration in PPy.¹⁵⁹ In the cycling of PPy films to potentials lower than -0.8 V , the currents are close to zero and down to -2.3 V (in AN solution) no peaks are observed because at these potentials the neutral film has low conductivity. At anodic potentials over $0.8–1.0 \text{ V}$, irreversible oxidation of PPy starts; it results in the loss of electrochemical activity and a drop in the conductivity of

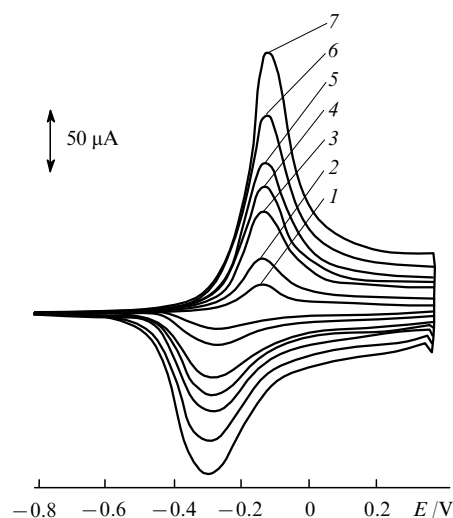


Figure 5. The cyclic voltammograms of 20-nm PPy/ BF_4 film in $\text{Et}_4\text{NB-F}_4/\text{AN}$ solution³² at varied scan rate 10 (1), 20 (2), 40 (3), 50 (4), 60 (5), 80 (6), 100 mV s^{-1} (7) (E vs. saturated calomel electrode).

the films.^{32, 35, 91, 160} The films can be repeatedly cycled without any sign of polymer degradation within a certain potential range where no side reactions occur (the so-called stability window); here the redox reaction of PPy is reversible.^{32, 35, 54, 107, 161}

A distinctive feature of VA of PPy films is, in the case of anodic oxidation, the steep anodic wave at the start of doping followed by a flat plateau. In the reverse scan of the potential, a cathodic wave appears at the end of the capacitive-type plateau; this wave is shifted in potential with respect to the anodic one. The current of the cathodic peak is usually lower than that of the anodic (whereas the surface areas of the anodic and cathodic parts of VA are the same). Such a behaviour is not typical of redox-active films. The theory predicts that thin redox-active films must show mirror-symmetric anodic and cathodic waves with identical peak potentials and currents.¹⁶² However, even the high quality films of conducting polymers manifest this potential shift between the anodic and cathodic peaks in their VA. The theory of redox-active polymers interprets such a behaviour as a kinetic effect of slow heterogeneous charge transfer.³²

The thermodynamic redox potential of the system is defined as the mean of the anodic and cathodic maxima ΔE_p (for the PPy film in Fig. 5 it is -0.2 V). As a first approximation, one can assume that the interaction between the charged segments of the polymer chains can be neglected and that there is only one redox state with a characteristic redox potential depending on the nature of the monomer unit. However, one must keep in mind that the redox potential of nominally the same system depends on the conditions of measurements and the regime of PPy synthesis (chemical nature and composition of the solvent and electrolyte, scan rate, thickness of the PPy film).^{32, 154, 163, 164} The redox potential of a polymer also depends on the time during which it was stored in a dielectric state.¹⁶⁵

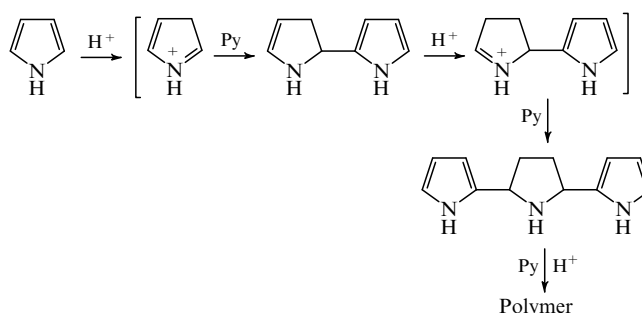
The interrelation between the Faradaic and capacitive processes in the course of reduction and oxidation is closely related to the redox mechanism. It was reported¹⁶⁶ that in CVA, the Faradaic oxidation associated with the charge transfer *via* interphase boundary is limited to the region of peaks, whereas the broad anodic plateau corresponds to the large capacity of the double layer at the surface (charge accumulation at the interphase boundary); the interphase surface is largely due to the porosity of the film. This problem remains debatable.¹⁶⁷ On the basis of the studies using impedance spectrometry and CVA, the following model for redistribution of charges in polymer was proposed.¹⁶⁸ In the electrochemical redox cycling of a polymer film, which is associated with penetration and removal of the anions, the polymer becomes subdivided in aggregates with the diameter about 6 nm. The capacity of the double layer formed reaches 200 F cm^{-2} . The capacitive behaviour of the conducting polymers is due the fact that they are porous and conductive and also due to the number of electroactive sites in the polymer not being fixed but dependent on the potential. The Faradaic charge results from the penetration of dopant anions into the aggregates, which is diffusion-controlled. The rate of the Faradaic process is lower than that of the capacitive.

The shape and parameters of VA are affected by a number of factors including the range of potential cycling, the scan rate, solvent used, composition of the electrolyte, film thickness, conditions under which it was prepared and its treatment and storage history. Synthesis under similar conditions does not always provide a possibility of obtaining similar VA of PPy films. Stirring of the solution of background electrolyte does not affect the shape of VA.³²

The shape of VA is indicative of the quality of PPy films. The rate of the charge transfer in conducting polymer and, therefore, its conductivity correlate with sharp anodic and cathodic peaks and narrow ΔE_p .^{103, 160, 169} The redox capacity of the film (the surface area under the anodic and cathodic branches of VA), in its turn, is related to the doping level of the polymer.^{32, 38}

The EP of pyrrole in galvanostatic regimes in the LiClO_4/PC system at low current density ($i \leq 0.3 \text{ mA cm}^{-2}$) yields PPy with a

high degree of conjugation (the energy of $\pi-\pi^*$ transition is 2.83 eV) and high doping level ($y = 0.37$), which shows narrow peaks in VA.⁶³ At high density of polymerisation currents ($i \geq 0.5 \text{ mA cm}^{-2}$), the VA of the polymer produced is distinguished by broad peaks, its doping level and degree of conjugation are low (the energy of $\pi-\pi^*$ transition is 3 eV). A similar effect of the EP current density on electrochemical properties of the polymer was reported in Ref. 81; overoxidation of the polymer at high anodic potentials of EP ($0.8-1.2 \text{ V vs.}$ saturated calomel electrode), results in reduced redox capacity of PPy films (Fig. 6). This effect is most pronounced in anhydrous electrolytes. It was supposed¹⁷⁰ that the decrease in conductivity is due to formation of saturated oligomers in the reaction initiated by the protons released in the oxidation of monomers near the electrode surface at high current density.



Addition of water to the electrolyte inhibits this reaction due to solvation of the protons.

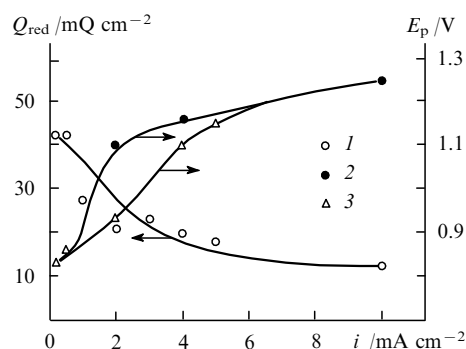


Figure 6. The dependence of anodic potential of polymerisation (E_p vs. saturated calomel electrode) and redox capacity (Q_{red}) of $1 \mu\text{m}$ PPy films on the current density (i) in galvanostatic electropolymerisation⁸¹ from solution of 0.1 M pyrrole + 0.1 M Bu_4NBF_4 in AN (1) with addition of 10 (2) and 50 (3) mM H_2O .

The thickness of a PPy film (and, correspondingly, charge in EP) is one of the major controlling parameters for VA of the films. The charge of reduction and oxidation of PPy during cycling (redox capacity) is proportional to the charge in synthesis. The redox capacity of PPy during cycling in AN comprises $8\% - 12\%$ of the EP charge in the Diaz electrolyte ($\text{AN} + 1\% \text{ H}_2\text{O}$) and up to 19% for EP in aqueous solution; this corresponds to a doping level of $20\% - 30\%$ in the former case and 47% in the latter.³⁸

An important electrochemical characteristic of the redox reaction on the electrode is the dependence of the anodic peak current i_{pa} on the scan rate v :

$$i_{pa} = Av^x,$$

where A is a constant and x is the exponent, which characterises the mobility of counterions in the PPy matrix. The redox reaction is controlled by the rate of electron transfer (adsorption, $x = 1$) for PPy films doped with small mobile anions (Cl^- , ClO_4^-) or in the opposite case of polymer doped with very bulky multicharged

anions (e.g., benzenetrisulfonate anion). For PPy films with medium-size anions (benzenesulfonate, toluenesulfonate) the electrode reaction is diffusion-controlled ($\alpha = 0.5 - 1$).^{46, 108} When the film thickness increases (over 1 μm), the electron transfer is superimposed by the diffusional restrictions, which result in broadening of the peaks in VA and their wider separation.^{32, 35, 46}

The VA of PPy films differ substantially when the latter are tested in aqueous media and aprotic solvents.^{88, 103, 107} In the former case, the currents are higher, owing to higher mobility of anions in the porous film. At the same time, the films synthesised in AN have better electrochemical reversibility of redox transition than those synthesised in aqueous electrolytes.^{36, 107} The former films are distinguished by a higher rate of electron transfer and narrower ΔE_p . The PPy films obtained in aqueous solutions are more porous and manifest higher capacitive currents in VA (their capacity is 460 F cm^{-3} compared with 390 F cm^{-3} for PPy synthesised in AN).³⁶

In the course of cycling, the PPy can exchange its initial dopant anion for another anion of electrolyte.^{88, 154, 155} The diffusion processes are controlled by the dimensions of the pores and the nature (dimensions, mobility) of the penetrating anion. The Cl^- anions in PPy/Cl^- upon cycling are replaced by the electrolyte anions F^- , ClO_4^- (Fig. 7).¹⁶⁴ In a solution of sodium poly(styrenesulfonate) (Na/PSS^-), PPy/Cl^- film loses its electroactivity as the anions of the polyelectrolyte are too large to penetrate into the film, while diffusion of Cl^- anions through the adsorbed layer of PSS^- anions is suppressed.

PPy synthesised in aqueous NaNO_3 solution, upon reoxida-

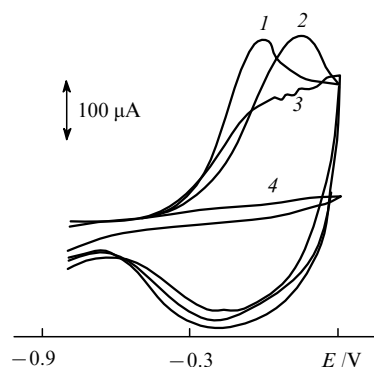
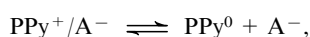


Figure 7. The voltammograms of PPy/Cl^- in 0.1 M aqueous solutions of: ¹⁶⁴ NaCl (1), NaClO_4 (2), NaF (3), NaPSS (4) (E vs. Ag/AgCl).

tion, manifests selectivity with respect to anions in the solution decreasing in the following series¹⁷¹ $\text{NO}_3^- > \text{ClO}_4^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$.

Active control of the ion transport is possible when the mobile species can be identified. The problem is complicated by the fact that several ionic species are often present in the system. There are two pathways for the charge transfer in the oxidation–reduction of the polymer^{46, 154, 155, 164, 172}



The former process implies diffusion of A^- anions away from the film upon reduction of oxidised polymer, while the latter, penetration of C^+ cations, which compensate the negative charge of immobile anions that become redundant after reduction of the polymer. Use of an electrochemical quartz microbalance provided a possibility of following the changes in the mass of the film during cycling in solution and, thus, of elucidating the nature of the ions penetrating into the film.^{88, 164, 173} The anionic transport predominates when small single-charged anions (Cl^- , ClO_4^- , H_2PO_4^- , NO_3^-) are used in electrochemical synthesis of PPy. In such a film,

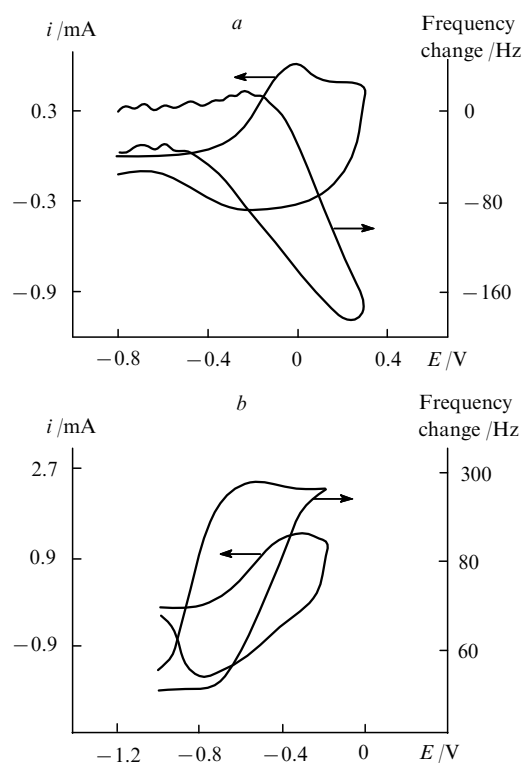


Figure 8. The changes in currents and frequency shifts of quartz resonators for the films:¹⁶⁴ PPy/Cl^- (a) and $\text{PPy}/\text{dodecyl sulfate}$ (b) in aqueous solution of 0.1 M NaCl (E vs. Ag/AgCl).

anions rather than cations penetrate into the film and are removed in the course of cycling. When the polymer is synthesised with bulky immobile anions, multicharged anions or polyelectrolytes [dodecylsulfate, toluenesulfonate, phthalocyanine tetrasulfonate, SO_4^{2-} , HPO_4^{2-} , poly(styrenesulfonate)], which are firmly fixed in PPy, then the cationic transport through the polymer–electrolyte boundary predominates. Figure 8 shows the VA of PPy/Cl^- and $\text{PPy}/\text{dodecylsulfate}$ films and also the change (decrease/increase) in the resonance frequency due to the changed (higher/lower) effective mass related to electrochemical processes.

The cationic transport also predominates in self-doped polymers where dopant anions are covalently bonded with the polymer matrix, e.g., poly{pyrrole-co-[3-(pyrrol-1-yl)propanesulfonate]}, and for a molecular PPy/Nafion composite where the dopant anion is polymeric.¹⁶⁴ The frequency response of these films depends on the nature of the cation of the electrolyte in which the films are tested.

For the $\text{PPy}/\text{SO}_4^{2-}$ film in an aqueous solution of CsCl, a mixed anionic–cationic transport is observed depending on the cycling potential.¹⁷³ The migration of cations into electrolyte prevails at the initial stages of oxidation of PPy/poly(styrenesulfonate), but upon further growth of the potential this process is complicated by the anionic counterflow.¹⁷⁴ The mixed type of charge transfer often results in the appearance of several peaks in anodic or cathodic parts of VA.^{107, 175}

The type of charge transfer is governed also by the choice of a solvent. The bulky dodecylsulfate anion is always firmly fixed in the PPy film synthesised in its presence, irrespective of the solvent used. However, the mobility of the ions in the bulk of the film during redox switching depends on the solvent. Upon reduction in AN, dodecylsulfate anions leave the film, whereas in aqueous solutions they remain trapped in the polymer matrix;^{176, 177} upon reduction, Na^+ cations are inserted into the film. The stronger interaction between the charged polymer chains and dodecylsulfate anions in aqueous solutions is due to the hydrophobic nature of the aliphatic part of the anion. For the polymer doped with the

highly mobile ClO_4^- anion, prolonged cycling in aqueous solution results in the cationic transport substituting for anionic.⁸⁸ In AN, the anionic transport prevails in this film.

The exchange of the dopant anion in the polymer can result in a changed type of ionic transport.¹⁵⁶ The ionic charge transfer can be controlled by creating in the polymer an ion pair of immobilised anion and multicharged cation of electrolyte.¹⁷³

The contribution of anionic and cationic charge transport strongly depends on the EP potential.^{178, 179} The redox switching in PPy synthesised at 1.0 V (vs. Ag/AgCl) are accompanied by simultaneous mass transport of anions and cations, whereas in the films prepared at lower potentials of EP, the charge transport is separated into either anionic or cationic regions. The cathodic shift of the first cycle of reduction in VA is related to the phase transition in the polymer and indicates that cations are inserted into the film. This was confirmed using an electrochemical quartz microbalance and X-ray emission analysis.¹⁰³ The potential of the anomalous reduction peak in the first reduction cycle of PPy film depends on the size of electrolyte cation (in AN solution).¹⁷⁷ During the first reduction cycle, a large uptake of electrolyte by the film is observed (up to 3 M). The measurements using impedance spectroscopy¹⁰³ showed that over several initial cycles the resistance of the PPy film drops (ionic conductivity grows) and remains virtually unchanged in further cycling. In reoxidation of the polymer, the uptake of the anions by the film exceeds the release of cations (the anionic type of the charge transport predominates); this results in formation of a non-equilibrium state in the polymer containing excess of the electrolyte. The mobility of the anions in such a polymer is greatly enhanced; the redox transition in AN solution proceeds fast only for the non-equilibrium form of the polymer. The PPy films prepared from aqueous solution with Et_4NClO_4 originally possess a high ionic conductivity. The strong difference between the ionic conductivity of the PPy films prepared from aqueous and AN solutions can be related to lower mobility of anions due to the better solvation of the polymer in aqueous solution.

Possibly, it is the excess of electrolyte in the film that causes wide scatter of the data for the diffusion coefficient of anions measured using different methods, 10^{-11} to 10^{-9} $\text{cm}^2 \text{s}^{-1}$ for ClO_4^- , BF_4^- in AN^{32, 34, 35, 37, 47} and 10^{-10} to 10^{-8} for Cl^- , ClO_4^- in aqueous solutions.^{108, 180, 181}

Since the properties of the polymer are to a large extent governed by the dopant anion, the choice of the latter depends on the properties to be imparted to the polymer. If hydrophilic anions such as ClO_4^- or BF_4^- are used in EP, the polymer produced also becomes hydrophilic, in contrast to PPy doped with hydrophobic polymeric counterions. In the latter case, sensitivity of PPy to humidity is greatly reduced. In the presence of optically active anions (e.g., camphorsulfonic acid), the polymer acquires optical activity, which can be used to separate chiral stereoisomers.⁶⁶ In order to prepare flexible and smooth films that easily detach from the electrode, organic dopant anions are used. Aromatic and bulky surfactant sulfonate anions provide better conductivity and stability of the polymers. Thin PPy films with small anions manifest the most pronounced electrochromic properties and the fastest response.^{182, 183} In order to make PPy coating with strong adhesion to aluminium electrode, hydroxyanthraquinonesulfonic acid is recommended, because it forms a complex with aluminium.⁶⁶

VII. Modification of the properties of polypyrrole films

Modification of the electrochemical properties of PPy is a promising and diverse field of research. This can be achieved using a variety of methods, viz. by the synthesis of polymer from pyrrole derivatives with corresponding electroactive substituents, by introduction of electroactive dopant anions, by modification of the film surface through immobilisation of certain reactants

thereon. These methods are supplemented by copolymerisation and preparation of PPy-based composites.^{184–186}

Numerous examples of preparation of PPy derivatives containing electro- and catalytically active groups are given in Ref. 187. The *N*-substituted PPy with grafted electroactive groups, derivatives of viologen,¹⁸⁸ anthraquinone,¹⁸⁹ and porphyrins of Co, Ni, Mn were studied.^{190, 191} The PPy with a covalently bonded three-nuclear ruthenium cluster showed high chemical and electrochemical stability, especially at positive potentials. This electrode was used for electrocatalytic oxidation of benzyl alcohol.¹⁹² The cluster $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$ was inserted in the electrode surface covered with the ion-exchange polymers based on *N*-substituted PPy.¹⁹³

EP of pyrrole with bulky alkyl substituents provides a route to prepare a polymer soluble in organic solvents. This facilitates its further processing, including preparation of coatings of well defined structure and thickness using the Langmuir–Blodgett technique.¹⁹⁴

Substitution in the monomer ring causes a decrease in the conductivity of PPy films.³² However, in many cases, the conductivity does not change strongly when dopant anion is replaced with another one.¹⁴⁹ Various organic and inorganic electroactive anions were used as dopants for PPy matrix; these include tetrathiomolybdate,^{195–197} tetrachloroferrate,^{151, 198, 199} ferrocyanide,^{61, 119, 155, 172, 200} metal phthalocyanines and porphyrins,^{73, 201–205} ferrocenesulfonates,^{206, 207} sulfonates of quinones,^{208, 209} isopolyanions,²¹⁰ heteropolyanions.^{211–216} A wide array of conducting polymers with various incorporated functional molecules is described in Ref. 217.

Studies on the growth of PPy in the presence of the above-mentioned anions and on the properties of the polymers obtained revealed a number of common features inherent in these polymers: (1) the rate of EP in the presence of multicharged anions is unusually fast; (2) it is difficult to replace electroactive anions in the polymer matrix with another anion; (3) ΔE_p shifts to the cathodic region; (4) the electroactivity of a polymer doped with electroactive dopant anions is substantially enhanced due to the inherent redox reaction of the anions incorporated in the polymer matrix. The enhanced electroactivity of the conducting polymers is a desirable feature for the ones to be used as electrode materials in rechargeable batteries.

The synthesis and electrochemical properties of PPy films doped with FeCl_4^- anions were discussed in Refs 198, 199. The introduction of tetrachloroferrate anions to the electrolyte at the stage of EP results in acceleration of the process and brings about enhanced coarseness of the PPy films formed.¹⁹⁸ Supposedly, the large FeCl_4^- anion, which is connected to the polymer matrix with hydrogen bonds,¹²⁰ decreases the Coulombic repulsion of two radical cations thus promoting the dimerisation. The incorporation of FeCl_4^- into PPy improves the reversibility of the redox transition and permits the synthesis of conducting films in galvanostatic regime without degradation of the polymer material even at high current density (2 mA cm^{-2} , further studies showed that the current density up to 8 mA cm^{-2} can be used). It was assumed on the basis of CVA studies¹⁹⁹ that due to the cage effect FeCl_4^- anions are reversibly reduced in the polymer matrix. This contributes to the redox capacity of the polymer. The VA of PPy/ FeCl_4^- films are stable in the course of cycling in acetonitrile solutions of Et_4NClO_4 and $\text{Et}_4\text{NFeCl}_4$, whereas in solution of NaClO_4 they are unstable. In AN/ $\text{Et}_4\text{NFeCl}_4$ electrolyte, the PPy/ FeCl_4^- films do not experience degradation even when the cycling range is extended to +1.5 V, the redox capacity of the films increasing more than threefold. The surface of PPy/ FeCl_4^- films is covered with crater-like¹⁹⁹ or dendrite-like structures¹⁵¹ depleted of FeCl_4^- anions.

The VA of PPy film doped with $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ anions shows two pairs of redox peaks,⁶¹ the additional pair near 0.1 V appears due to the reversible redox transition $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$. The PPy film doped with $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ is more electroactive than PPy/ ClO_4^- , its redox capacity is higher, the current

peaks are sharper and are shifted to more negative potentials. Upon cycling of $\text{PPy}/\text{Fe}(\text{CN})_6^{4-/3-}$ in a broad range of potentials including the region of redox reaction of the polymer, the NO_3^- anions of electrolyte substitute for $\text{Fe}(\text{CN})_6^{4-/3-}$. When the cycling range is restricted to the oxidised state of the polymer, this system behaves as a conducting ion-exchange membrane. Oxidation (reduction) of $\text{Fe}(\text{CN})_6^{4-/3-}$ immobilised in the polymer matrix is accompanied by migration of the cations of electrolyte from (into) the film.¹⁵⁵ The $\text{Fe}(\text{CN})_6^{4-}$ anions leave the film at potentials more negative than -0.4 V for thick and -0.6 V for thin films.¹⁷² Reduced PPy contains, in addition to ferrocyanide anions, cations that neutralise the anionic charge. At the same time, there are indications²⁰⁰ that cations penetrate the film already at the stage of synthesis, because each positive charge of the polymer matrix is compensated with a multicharged ferricyanide anion. X-Ray diffraction revealed that $\text{PPy}/\text{Fe}(\text{CN})_6^{4-}$ has a more regular structure than PPy doped with single-charged anions.¹¹⁹ Mössbauer spectroscopy showed that PPy film prepared at anodic potential of 0.75 V (vs. saturated calomel electrode), when the ferrocyanide–ferricyanide transition must have occurred, contains only $\text{Fe}(\text{CN})_6^{4-}$ anions.¹¹⁹ In other words, the charge is redistributed between the anions and polymer matrix.

The PPy/ferrocenemonosulfonate (PPy/FMS) and PPy/ferrocenedisulfonate (PPy/FDS) showed²⁰⁶ a higher redox capacity and lower electrochemical stability than $\text{PPy}/\text{ClO}_4^-$. The PPy/poly(vinylferrocenesulfonate) films (PPy/PVFS) are smooth and uniform; the anion immobilised in the film is retained for hundreds of cycles. The maximum discharge capacity of a Li/PPy/PVFS battery was 120 A h kg^{-1} . The PPy/PVFS is a promising electrode material for rechargeable batteries. The instability of PPy/FMS and PPy/FDS is related to degradation of PPy, because in the region of redox transition of ferrocenesulfonates (0.7 – 1.2 V vs. Ag/AgCl) overoxidation of PPy can occur. In order to reduce the redox potential of ferrocenic (F) dopants, the polymeric dopant, poly(styrenesulfonate-co-vinylferrocene) (PVFSS) was synthesised.²⁰⁷ In this polyanion, sulfogroup is not directly bonded with the ferrocene ring. PPy/PVFSS showed two pairs of redox peaks, at -0.1 V and $+0.35$ V (vs. Ag/AgCl), which correspond to PPy/PPy^+ and F/F^+ transitions. The latter transition is shifted by 0.4 – 0.5 V to cathodic region as compared with PVFS. The zinc battery with PPy/PVFSS showed a higher (1.5 times) discharge capacity and energy density and improved charging–discharging performance compared with a lithium cell. Its Coulombic efficiency remained unchanged during 500 cycles.

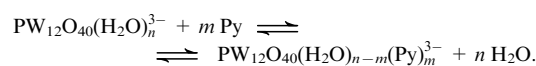
The preparation, composition and electrochemical properties of PPy films incorporating quinoid dopant anions was reported in Ref. 208. The redox transitions of the quinone/hydroquinone pair of tiron (T), naphthoquinone (NQ) and anthraquinone (AQ) are superimposed on the large background signal of PPy. The position of the redox pair of quinones on the potential axis depends on the dimensions of their conjugated π -systems; $\Delta E_T > \Delta E_{NQ} > \Delta E_{AQ}$. The electrochemical properties of their redox transition are similar to those for quinones adsorbed on the electrode. The redox capacity for AQ on the electrode reaches its limiting value, whereas for PPy/AQ it grows linearly with increasing charge in EP. The PPy/NQ film is highly stable, its VA did not change after a four-days' storage in electrolyte. The electrocatalytic oxidation of ascorbic acid was performed on a PPy/NQ electrode. Tiron plays the role of both a catalyst and dopant in EP of pyrrole ($\Delta E_T = 0.605$ V vs. saturated calomel electrode at pH = 1); initially it is oxidised to quinone and the latter oxidises pyrrole to a radical cation that initiates polymerisation. The charge–discharge properties of PPy/AQ, PPy/NQ and PPy/ ClO_4^- films synthesised at the same charge of EP in the system of $0.1 \text{ M Et}_4\text{NClO}_4/\text{AN}$ at 0.02 mA cm^{-2} were investigated.²⁰⁹ For PPy/AQ, the charge–discharge capacity (119 mQ cm^{-2}) and charge density (150 A h l^{-1}) more than twice exceed respective values for PPy/NQ and PPy/ ClO_4^- . The choice of an electrolyte plays an important role; Li^+ cations in aprotic solvents form

insoluble compounds with dianions of quinoid derivatives and this makes the redox transition irreversible.

The incorporation of metal porphyrins (MP) and phthalocyanines (MPHC), isopoly- and heteropolyacids (HPA) into the matrix of a conducting polymer can be useful for electrocatalysis. The immobilisation of catalysts in the films of conducting polymers provides a number of advantages over monolayers of catalysts grafted to or adsorbed on a support. First, the surface concentration of the catalyst can be electrochemically controlled due to the mechanism of polymerisation inherent in conducting polymers; the second is that the active form of the catalyst can be easily regenerated.

The effect of the nature of isopolymolybdate species on EP of pyrrole and aniline and the electrochemical behaviour of the polymer films doped with polymolybdate anions were investigated using CVA.²¹⁰ The number of molybdenum atoms in the polymolybdate anion that predominates in solution and is incorporated as a dopant in the growing polymer film was controlled through the ratio of acid and molybdenum in electrolyte. The polymolybdates promote the film growth and, owing to their intrinsic electrochemical activity, enhance its redox capacity. In the course of cycling polymer films, the polymolybdate anions are easily removed to the electrolyte from PPy, whereas they remain firmly immobilised in PANi due to formation of complex.

The electrochemical properties of Keggin-type tungstates and molybdates, the effect of pH on the properties of HPA and stability of HPA derivatives in strongly acidic aqueous solutions were studied in detail.²¹⁸ Pyrrole (and similarly, aniline) in aqueous and AN solutions forms soluble complexes with HPA, where it substitutes the co-ordinated water molecules



EP of these complexes results in formation of PPy films doped with anions of HPA.^{211, 212, 214} The VA of these films are distinguished by the reversible peaks of the polymer itself and of multistep reversible redox transitions of HPA. The electrochemical behaviour of HPA immobilised in the polymer differs from the behaviour of the same HPA in solution due to low conductivity of PPy and poly(*N*-methylpyrrole) (PNMPy) in the potential range of HPA reduction.²¹¹ The peaks of HPA are characterised by diffusion-controlled charge transport. Since HPA anions are firmly immobilised within the film, the charge transport involves the Li^+ cations. The maximum doping level for PPy is ²¹⁴ 27% for $(\text{PMo}_{12}\text{O}_{40})^{3-}$, 26% for $(\text{PW}_{12}\text{O}_{40})^{3-}$, 23% for $(\text{SiW}_{12}\text{O}_{40})^{4-}$. The conductivity of the PPy/HPA films is 2.6 S cm^{-1} ; PNMPy/HPA, $5 \times 10^{-3} \text{ S cm}^{-1}$. The comparatively high conductivity (taking into account the very high molecular mass of HPA) can be explained by the contribution of a number of factors. First, the delocalisation of the negative charge in HPA anion facilitates the uniform charge distribution along the polymer chain. This factor also facilitates formation of the polymer with a more regular structure. And finally, the HPA anions can play the role of charge carriers between the polymer chains.

According to Ref. 212, PPy must be prepared from fresh aqueous solutions of HPA because fast trimerisation of pyrrole in solution results in formation of PPy films with poorly reproducible properties. Use of aqueous solutions with neutral salts of HPA allows one to prepare PPy with high conductivity and stable electrochemical properties. The PANi/HPA films are also stable in acidic solutions. The EP of pyrrole in aqueous solutions of Dawson-type HPA (which have the dimensions two times larger than the Keggin-type HPA)²¹⁵ and of aniline in AN solutions of these HPA²¹³ also yields electroactive and highly stable polymers. The redox capacity for PPy/ $\text{P}_2\text{W}_{18}\text{O}_{62}^{6-}$ was²¹⁵ 50 mA h g^{-1} (or 190 mA h cm^{-3} , as the density of the film is very high, 3.9 g cm^{-3}). The incorporation of HPA anions in conducting polymers brings about substantial changes in their electrocatalytic and catalytic properties²¹⁹ due to interactions with the polymer matrix and molecular dispersion of the anions. In the case of PANi

doped with HPA ($\text{PMo}_{12}\text{O}_{40}^{3-}$, $\text{PMo}_{11}\text{Fe}^{2+}\text{O}_{39}^{4-}$, $\text{PMo}_{11}\text{Mn}^{2+}\text{O}_{39}^{4-}$), an enhanced selectivity in formation of acetone in catalytic decomposition of propan-2-ol was observed.²¹⁶ In catalytic conversion of ethanol on PAni/ $\text{PMo}_{12}\text{O}_{40}^{3-}$, mainly acetaldehyde is formed (redox activity), whereas on PAni/ $\text{PW}_{12}\text{O}_{40}^{3-}$ and PAni/ $\text{SiW}_{12}\text{O}_{40}^{3-}$, ethene is the main product (acid–base properties).²²⁰ The activity of the catalysts depends on the preparatory procedure for PAni/HPA.

The PPy films modified with MPhC ($M = \text{Fe}, \text{Co}$) showed high electrocatalytic activity in electroreduction of oxygen^{201, 203, 204} and those modified with MP, in the oxidation of phenol derivatives.²⁰⁵ Reduction of thionyl chloride was performed on PPy electrode modified with iron tetrasulfophthalocyanine.²²¹ The introduction of MPhC in the PPy matrix brought about enhanced currents of thionyl chloride reduction, compared with a PPy/ ClO_4^- electrode and even with a platinum one. The reaction mechanism was not changed. Apparently, the enhancement of currents is due to elevated concentration of adsorbed SOCl_2 on the electrode surface, owing to formation of complexes with MPhC.

PPy was also modified by non-ionic species, in particular metals,²²² metal oxides,^{223–225} and enzymes.^{226, 227} On a PPy film with peroxidase, direct bioelectrocatalysis of cathodic reduction of hydrogen peroxide was observed.²²⁷

VIII. The potential for polypyrrole applications

The PPy is a promising material for rechargeable lithium batteries.^{228–230} The advantages of the polymeric electrodes include light weight combined with high energy storage capacity and a possibility to manufacture and use them in the form of thin films. Table 3 summarises some parameters of the polymer-based lithium batteries and, as a reference, also the properties of lead and nickel–cadmium batteries.²³¹

Table 3. Comparison of characteristics of some electrochemical batteries.²³¹

Battery	U /V	W /W kg ^{−1}	Q /A h kg ^{−1}	E /W h kg ^{−1}
PAC/PC, LiClO ₄ /Li	3.7	3.5	105	80
PAC/PC, LiClO ₄ /PAC	3.0	1.1	85	50
PPh/PC, LiClO ₄ /Li	4.4	7.0	–	80
PPy/PC, LiClO ₄ /Li	3.2	2.8	85	55
PTh/PC, LiClO ₄ /Li	3.4	2.5	75	50
PAni/PC, LiClO ₄ /Li	3.3	0.4	–	60
Lead	2.1	1.2	–	40
Nickel–cadmium	1.35	–	–	35

Note. PAC is polyacetylene, PPh is polyphenylene, PPy is polypyrrole, PTh is polythiophene, PAni is polyaniline, PC is propylene carbonate.

A comparison of energy storage capacity shows that polymer-based batteries are superior. Note also that Li/PPy batteries have a high Coulombic efficiency. In addition to the energy storage advantages, the conducting polymers provide also operational ones. During discharge of the battery, the polymers do not dissolve and this eliminates the problem of the changes in the electrodes' shape in the solution–deposition cycles. The flat discharge that usually destroys conventional batteries is not dangerous in the case of conducting polymers. However, there are certain problems associated with the use of conducting polymers in batteries. First, in the course of charge–discharge, the bulky ions enter and leave the polymer film giving rise to mechanical stresses; this brings about the problem of mechanical integrity of the polymeric electrodes during their operational life. Second, the use of a lithium electrode requires high purity of the electrolyte and perfect sealing of the battery in order to prevent

penetration of water or oxygen into it. A battery with PPy/ Cl^- cathode and PPy/polyvinylsulfate anode was developed;¹⁵² the discharge of the battery is accompanied by removal of Li^+ ions from the anode and Cl^- anions from the cathode. Upon charging, these ions again are inserted into the electrodes. An all-solid rechargeable lithium battery with electrolyte based on polyacrylonitrile extended with organic solvent has been proposed.²³⁰

Amorphous MoS_3 is often used as a cathodic material in lithium batteries.²³² Yet, its conductivity is exceedingly low, $5.2 \times 10^{-4} \text{ S cm}^{-1}$, and a conductive carbonaceous additive must be used. Introduction of MoS_3 into the PPy matrix in the course of EP of pyrrole in the presence of ammonium tetrathiomolybdate provided a possibility of enhancing the conductivity of thin-film MoS_3 electrodes to 2.6 S cm^{-1} (see Refs 195, 196). The VA of PPy/ MoS_4^{2-} film shows a shift of ΔE_p by 200 mV to the cathodic region; this is a typical feature of immobilised anions. The capacitive currents are low, cations take part in the charge transport. The EP of pyrrole from aqueous KCl solution on the substrate matrix Pt/ MoS_3 results in the formation¹⁹⁷ of a film having electrochemical behaviour typical of the polymers doped with small anions and with a higher ionic conductivity than that of PPy/ MoS_4^{2-} . Apart from MoS_3 , for rechargeable lithium batteries, the PPy/ V_2O_5 ²²⁴ and PPy/ MnO_2 ^{223, 225} composites were used as cathodic materials.

PPy doped with alkyl naphthalenesulfonates was used in an all-solid electrolytic capacitor with aluminium electrodes.²³³ The PPy was prepared by EP on the surface of anodised aluminium foil that was preliminarily covered with a thin layer of pyrolytic MnO_2 . Substantially improved thermostability of the capacitor (1000 h at 120 °C) was achieved by means of introduction of nitrophenol in the electrolyte at the stage of pyrrole EP. The properties of this capacitor were superior compared to the common aluminium electrolytic, multilayered ceramic and tantalum capacitors with solid electrolyte and the thin-film organic ones.

The electric conductivity of the conducting polymers is sensitive to chemical agents; this provides a possibility of developing various sensors based on them. It was reported that PPy can be used as a sensor for certain components in gas mixtures, including both inorganic (NO , CO_2 , CO , NH_3 , H_2S)^{234, 235} and organic (acetone, methanol, ethanol)²³⁶ compounds.

The amperometric biosensors based on PPy with incorporated enzymes such as glucose oxidase,^{237, 238} alcohol dehydrogenase,²³⁹ glutamate oxidase and peroxidase²⁴⁰ can find extensive applications. The electrocatalytic activity of the glucose oxidase was enhanced by the introduction of a redox mediator, tiron, and a polymeric dopant, alton (a water-soluble analogue of Nafion).²³⁸ The latter, owing to the high content of fluorine in the polymer, enhances solubility of oxygen and thus promotes oxidation of glucose. In the near future, one might anticipate development of preparations on the basis of PPy, by EP of monomers with grafted enzymes or drugs.²⁴¹ Since PPy is biocompatible and non-toxic, it is possible, by electrochemical reduction of oxidatively doped polymer, to controllably supply an organism (cell) with microscopic doses of a drug that has been immobilised in ionic form, e.g., glutamate, aspartate, dopamine.^{242, 243} Separation of some drugs using PPy was reported;²⁴⁴ caffeine and theophylline are selectively absorbed by PPy, whereas protein molecules are not. PPy can be used as an efficient conductor in biological media (e.g., for regeneration of a nerve tissue).²⁴⁵

A promising field is the application of PPy as a protective coating for semiconducting anodes in photoelectrochemical cells. Usually, when photochemical reactions on inorganic semiconductors are carried out in humid media, the surface of semiconductor rapidly oxidises and electrodes become inoperative. The PPy film covering semiconductor prevents passivation of its surface and simultaneously allows formation of the electron holes, which pass to the polymer (in other words, the electrochemical reaction will now occur on the polymer surface). Such systems were studied for GaAs,²⁴⁶ CdS,^{56, 57} CdSe.⁵⁷ Photochemical cells with solid poly-

electrolytes were developed.²⁴⁷ The photoelectrochemical oxidation of water could be performed by combining the photoeffect on PPy-film-protected CdS^{56, 57} and CdSe⁵⁷ with electrocatalysis on RuO₂, Pt, Rh particles dispersed in the polymer.

Flexible films of conducting polymers can be used as protective electromagnetic shields.^{3, 248} For example, 50- μ m-thick PPy films provide 30-dB attenuation; in many cases, this is sufficient for practical applications.²⁴⁹

The PPy films electrochemically deposited onto a surface of porous silicon were used as electrical contacts in the structure of an electroluminescent diode.²⁵⁰

The PPy antistatic coatings on synthetic polymer fibres (polyethylene,^{251, 252} nylon²⁵³) were produced by polymerisation from gas with the oxidants (iron and copper salts) applied onto the fibre surface.

Microscopic electrochemical transistors were prepared²⁴³ by means of electrocopolymerisation of pyrrole and *N*-methylpyrrole between microelectrodes (emitter and collector) separated with a narrow slit. The conductivity of the polymer channel can be controlled by varying the voltage applied to the auxiliary control electrode. The latter was embedded in a solid or fluid polymeric electrolyte placed over the conducting polymer coating.

The capability of the polymer to reversibly change its volume in the range from 1% to 100% upon electrochemical doping was used²⁵⁴ to make 'electrochemical muscles' based on bilayered strips comprising PPy and polyethylene layers. Upon doping, the free end of the strip strongly deflected from its initial position and returned back upon dedoping.

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Boron and its compounds with nonmetals: chemical bonding and the electronic properties

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Abstract. Theoretical and experimental data on the electronic structure, chemical bonding, and charge distributions in condensed boron and solid-phase boron compounds with a number of *sp*-elements are reviewed. The applicability of quantum chemistry methods to a description of the physicochemical properties of boron and borides of nonmetals, as well as prospects of using computational methods in the theoretical materials science of borides, are discussed. The bibliography includes 452 references.

I. Introduction

Boron and its compounds with *sp*-nonmetals form an important class of chemical substances of great scientific, industrial and commercial importance, due to their unique physicochemical properties. Their well known application fields include synthesis of chemically inert and refractory borides, abrasives, dopants to heat-resistant alloys, components of multi-purposes ceramic materials, nuclear energy (boron), elements of cutting tools, composites, abrasives (boron carbides), high-temperature ware, semiconducting devices, chemical engineering (nitrides, phosphides, and arsenides), important precursors for the preparation of other numerous boron compounds (oxides).

Here lies the main reason for an intense development of the synthesis of novel, more complex boron-containing phases and materials, as well as for studies of their crystallography, thermodynamics, and other physicochemical properties, like electromagnetic, thermal, *etc.* Extensive experimental data obtained in these studies are presented in numerous original publications and summarised in a number of fundamental reviews and monographs.^{1–41}

Recently, substantial progress in the investigations of the electronic structure and chemical bonding in the compounds under discussion was achieved using advanced computational quantum chemistry methods. The aim of these studies was to

gain insight into the particular properties of different borides on a microscopic level, including interpretation of experimental physical chemistry data, and direct theoretical modelling of structures and properties of the novel boron-containing compounds and materials.

In this paper, we have attempted to discuss the state-of-the-art and some prospects for computational solid state quantum chemistry studies of the fundamental electronic properties of boron and its compounds with nonmetals. Emphasis was placed on the most widely studied boron compounds such as carbides, nitrides, carbonitrides, B-containing nanostructures, as well as on boron phosphides, arsenides, and oxides.

Results of quantum chemistry calculations are discussed with the use of experimental (mainly spectroscopic) data that give additional information on the electronic structure of these phases.

II. Chemical bonding and electronic structure of condensed boron

1. Crystalline boron

Among few other elements, boron forms a wide range of various phases in solid state. More than 10 polymorphous crystal modifications of boron may be prepared under specific conditions (temperature, pressure, various impurities, *etc.*).^{1–8, 17, 22–25, 32, 36–42}

Up to now, three most stable forms of solid boron with the known crystal structures were obtained unequivocally: α -rhombohedral B₁₂, α -tetragonal B₅₀, and β -rhombohedral B₁₀₅. There are several indications of other forms, such as β -tetragonal B₁₉₂ and orthorhombic phases detected at high temperatures ($T \sim 1500$ K).^{37–42} Crystal structures of these phases differ in the arrangement of B₁₂ icosahedra, which are the fundamental building blocks of boron phases.

According to^{1, 8, 28, 32, 36, 43}, the crystallographic and physicochemical properties of crystalline boron are defined by electronic structure of isolated boron atom, which has s^2p^1 valence electron configuration. This configuration is unfavourable, and it should transform to the more stable s^1p^2 when the solid state is formed (the transformation proceeds as a one-electron transition $s^2p^1 \rightarrow s^1p^2$). For the latter configuration further transition can occur according to the scheme: $s^1p^2 + s^1p^2 \rightarrow s^1p^3 + s^1p^1$. Therefore, in the real modifications of crystalline boron a number of $s^x p^y$ electron configurations due to electronic exchange between

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boron atoms is possible. Since the relatively stable electron configurations in multi-particle system can be achieved in many ways, a variety of crystal structures with different properties might be formed.

Below we consider the results of quantum chemistry computations of electron energy spectra for the different forms of solid boron.

Rhombohedral α -B₁₂. The unit cell of α -rhombohedral boron (α -B₁₂) with parameters $a = 5.057$ Å and $\beta = 58.10^\circ$ consists of 12 boron atoms.^{44–48} The basic polyhedron is an icosahedron conjugated with the neighbouring icosahedra (Fig. 1a). High precision structural studies of α -B₁₂ indicate slight distortions of ideal B₁₂ polyhedra due to the Jahn–Teller effect, which lowers its symmetry from I_h to D_{3d} .

The problem of interatomic interactions and stability of the B₁₂ icosahedron, the main building block of crystalline boron, was considered for the first time by Longuet–Higgins and Roberts⁴⁹ in terms of molecular orbital (MO) theory. Using theoretical group analysis orbitals of B₁₂ were classified into irreducible representations. Two main blocks of MOs were defined depending on their spatial orientation. The first block consists of hybrid sp -MOs that are responsible for the ‘intracluster’ bonding. The second block includes B $2p$ -like orbitals oriented outside the cluster moiety that in turn are subdivided into bonding and non-bonding ones. The sequence of filling of the MO system in the overall B₁₂ spectrum places only 2 electrons on ‘outer’ bonding orbitals. In terms of the common theory of covalency, this fact

attests to the instability of the isolated icosahedron hindering formation (under normal conditions) of boron crystal structures of high symmetry with low coordination number (n). According to the estimates,⁴⁹ the electronic configuration of boron atoms in the icosahedron is close to the s^1p^2 in contrast to s^2p^1 configuration for the isolated boron atom.

The assumptions made in Ref. 49 were confirmed in later studies,⁵⁰ where a qualitative scheme of orbital configurations and interparticle interactions in solid α -B₁₂ is compared to that in isoelectronic Al metal.

Quantitative estimates of MO energies and compositions for isolated B₁₂ fragments were performed using cluster quantum-chemical approaches. The scattered waves X_α method (X_α SW) was applied to the studies of the electron energy spectrum (EES) of the icosahedral B₁₂.⁵¹ In the calculations interatomic B–B distances were varied in the range of 1.75–2.05 Å. The equilibrium value of 1.96 Å⁵¹ was determined using the total one-electron energy of the fragment, which exceeds the experimental value for α -boron by 10%.^{44–48, 52} This inconsistency may be due to the fact that the model cluster has an open outer shell, which is in agreement with its chemical instability.

Chemical bonding in crystalline boron has a delocalized and electron deficient nature.⁵³ Taking this into account, an empirical ‘ $3n+2$ ’ rule (where $n = 12$) was formulated⁵³ stating that two additional electrons are needed for a closed electron shell to stabilise the crystalline boron and the higher borides containing B₁₂ icosahedra as the structural elements.

The calculated MO diagram⁵¹ (Fig. 2) is in good agreement with a qualitative scheme.⁴⁹ The cluster states may be subdivided into bonding (oriented to the neighbouring centres) and non-bonding (directed to the outer parts) states. The energy gap between the T_{2u} HOMO and the H_g LUMO (‘forbidden zone’) obtained with transition state formalism⁵⁴ is 1.6 eV. It is close enough to the experimental estimate of this value in α -B₁₂.⁵⁵

The MO system of B₁₂ group, similar to that obtained in study⁵¹, was reproduced under the tight binding (TB) approximation.⁵⁶ The probable interactions between bonding and non-bonding states were neglected.^{57, 58} The calculated values of equilibrium interatomic distances and bonding energies are 1.85 Å and 5.7 eV atom^{–1}, respectively. Electron energy spectra for a number of isolated atomic polyhedra B₄, B₆, and B₁₂ were also simulated using extended Hückel (EH)⁵⁹ and Hartree–Fock (HF) methods.⁶⁰

The dependence of EES transformations for boron micro-particles on their geometry and dimensionality was studied by X_α

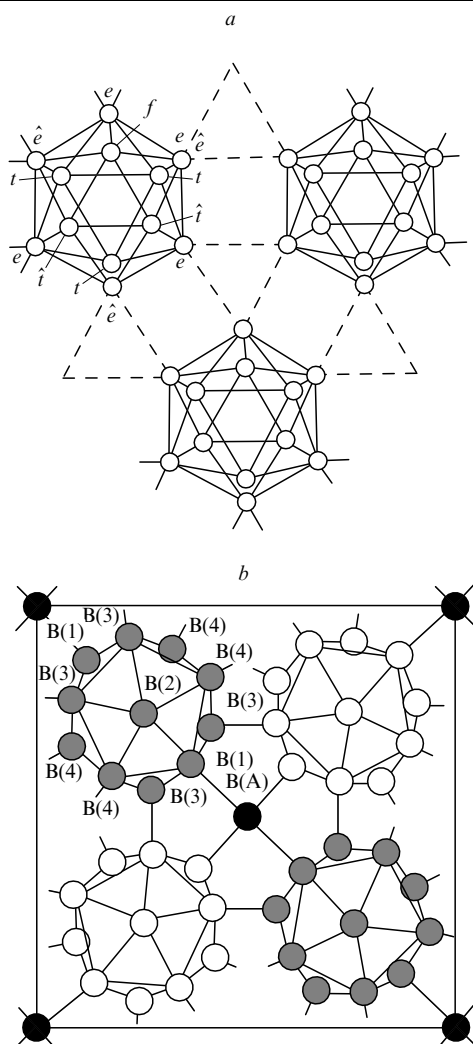


Figure 1. Fragments of crystal structures for (a) α -B₁₂ and (b) α -B₅₀.

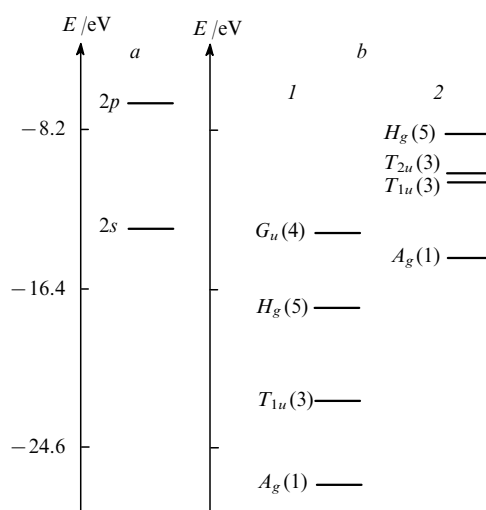


Figure 2. Energy levels (E /eV) of (a) boron atom and (b) B₁₂ icosahedron; (1)—bonding, (2)—antibonding orbitals; the values in brackets are degeneracies of the corresponding MOs.

SW method [clusters with nuclearity $n = 0, 1, 2, 3, 4, 6$; i.e. $B(0)$, B_2 (D_{∞}), B_3 (D_{3h}), B_4 (T_d), and B_6 (I_h) that contain only structurally identical centres were considered].⁶¹ The touching spheres approximation was applied; the exchange correlation parameters were taken from the published tables.⁶² The results of calculations indicate the presence of vacant p -states in the MOs system of the clusters, so they should have a prominent acceptor character and require introduction of additional electrons to achieve a stable configuration.

As it was pointed out,⁶¹ an increase in the n and valence electron concentration (VEC) results in an increase in the width of the occupied band. During this process, redistribution and delocalisation of atomic s - and p -states occur (since delocalized chemical bonds are formed), and the average one-electron energy (per boron atom) changes

$$\varepsilon \approx \frac{1}{N} \sum_i n_i \varepsilon_i,$$

where N is a number of atoms in the cluster, n_i is occupancy and ε_i is the energy of the i th orbital. For instance, energy values for B_2 and B_6 are 25.6 and 33.8 eV, respectively. These results indirectly support higher stability of high-coordinated structures of boron⁶¹ and its compounds.⁶³

The instability of the ideal B_{12} icosahedron was explained⁶⁵ by possible Jahn-Teller distortions due to a partial filling of degenerate higher orbitals.⁶⁴ In the calculations, a molecular dynamics method using the non-empirical Car-Parrinello scheme⁶⁶ under local electron density approximation (LDA)⁶⁷ was applied. The simplest version of this scheme was applied⁶⁸ to the reduction of icosahedral symmetry $I_h \rightarrow D_{3d}$.

Basic concepts of the method are given in Refs 69–73. The existence of a local minimum of $E(\varphi, R)$ (where φ is a wave function and R are atomic coordinates) for a polyhedron of C_i symmetry typical of boron crystalline compounds was established by the total energy minimisation method.⁶⁵ The maximum stability corresponded to the 'open' cluster framework B_{12} with C_i symmetry (Fig. 3), that possesses the minimum energy $\Delta E = E(C_i) - E(C_s) = 0.62$ eV. In the latter case, despite the decrease in the number of interatomic bonds from 30 (C_i) to 27 (C_s), the stability of the C_i form of B_{12} is higher due to the absence of the 'outer' non-bonding cluster orbitals (Fig. 4).

The first band theory calculation of crystalline α - B_{12} was performed by Perrot⁷⁴ using the muffin-tin orbitals (MTO) method⁷⁴ and Cohn–Sham potential parameters.⁷⁶ The calculations were done for 14 k -points in the irreducible part of the Brillouin zone (IPBZ) (Fig. 5). Bands energy dispersion in the direction $G \rightarrow Z$ is shown in Fig. 6. According to calculations,⁷⁴ 18 low energy bands are filled and separated from the lowest unoccupied bands by a forbidden gap (FG) with an energy of indirect transition $\Delta E_g = 2.88$ eV. This value is in accordance with experimentally proved non-metallic behaviour of α -boron.^{37–41}

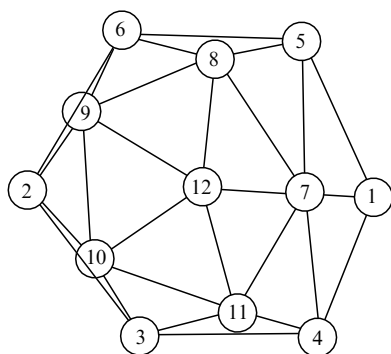


Figure 3. Optimised structure of B_{12} polyhedron in α -boron structure with atom numbers (1–12).

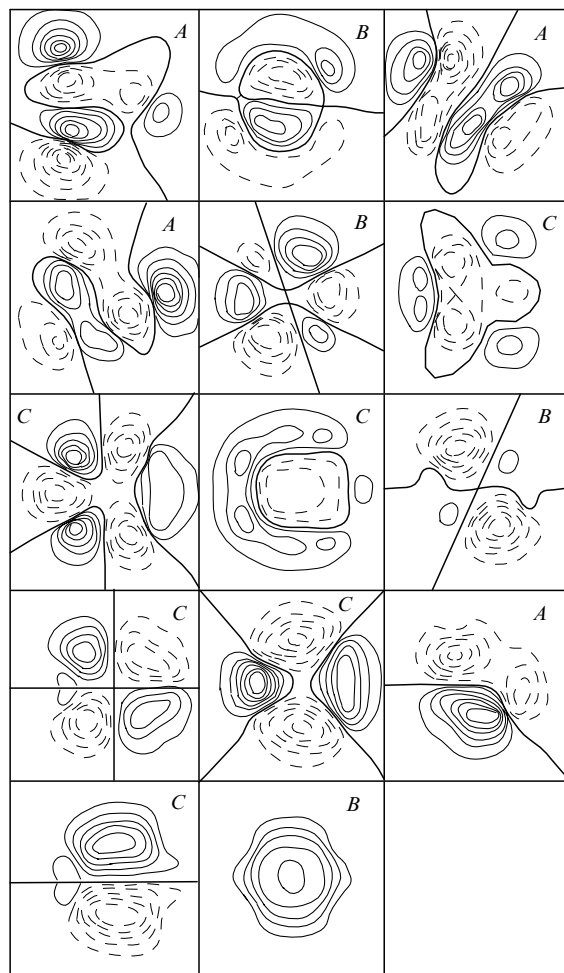


Figure 4. Wave function profiles of the optimised B_{12} structure [lower left part of the polyhedron; planes going through the atoms 1, 7, 12, 2 (A); 3, 6, 8, 11 (B); 4, 5, 9, 10 (C) as in the Fig. 3].

It is noteworthy, that the width of the filled band d (9.87 eV)⁷⁴ is significantly lower than the value 15.5 eV obtained from X-ray emission spectroscopy (XES) measurements.⁷⁷ The reason for this inconsistency lies in the application of the touching spheres model to loosely packed structures like α - B_{12} (in this case, it is necessary to take into account non-muffin-tin corrections) and also in the neglected correlation effects, which, as it is known,⁷⁸ may strongly

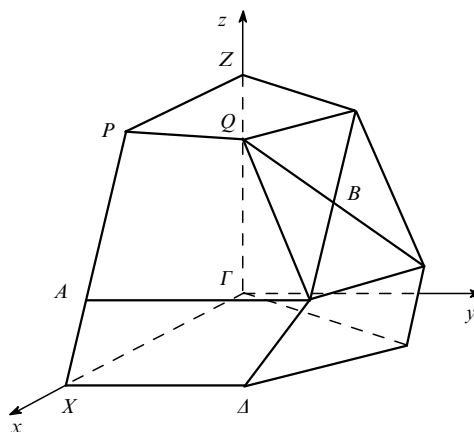


Figure 5. Irreducible part of the Brillouin zone for α - B_{12} .

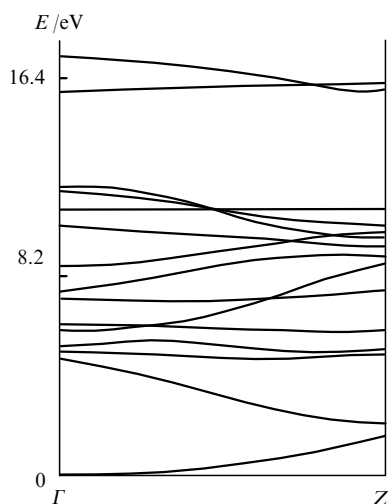


Figure 6. Energy bands for α -B₁₂ (E, eV).

influence the width of the forbidden zone. Minimisation of the intersphere region (structural factor S was varied in the range of 1.25–1.50 R_{MT} , where R_{MT} is muffin-tin radius) has lead⁷⁴ to a noticeable increase in both FG (5.33 eV) and the valence zone width (16.13 eV): the latter appeared to be substantially closer to the experimental values.

According to the data of non-SCF calculations using augmented plane waves method (APW)⁷⁹, α -B₁₂ should exhibit semi-

conducting properties. A qualitative scheme of interatomic bonds in α -boron based on the analysis of the energy dispersion was proposed. This scheme includes bonds of a boron atom with five nearest neighbours in the B₁₂ fragment and two- and three-centre bonding interactions with boron atoms of the neighbouring polyhedra.

The energy band structure of α -rhombohedral boron was also calculated by the pseudopotential method⁸⁰ with Bassani and Brust parameters.⁸¹ Initial calculations gave the value $\Delta E_g = 5.0$ eV, which is noticeably higher than the experimental value 2.0 eV (see Refs 82, 83) obtained from optical absorption data. Further fitting was performed by cutting of the potential $y(q)$ at $q = 3.2$ (a.u.)⁻¹, and satisfactory agreement with experimental data was achieved for $q = 3$ k_F [where $k_F = 1.2$ (a.u.)⁻¹ (see Ref. 84)]. A more precise *ab initio* calculation of a crystal built of B₁₂ fragments was done using a basis set of 2870 plane waves.⁸⁵ Both energy functions $E(k)$ and equilibrium interatomic distances were obtained. Analysis of the dispersion curves $E(k)$ lead to the values of 1.427 eV for indirect transition across a forbidden zone (between the top of valence zone X and the bottom of the conduction zone Γ), and -1.780 eV for the direct forbidden zone (in Γ point).

Charge distribution patterns in the planes defined by centres of icosahedra and by three independent faces of B₁₂ (Fig. 7) are quite informative. Additional charge density is concentrated on the atoms along the z axis indicating larger contribution of these atoms to chemical bonding in the icosahedron compared to the atoms in the (100) plane. It was concluded⁸⁵ that intracluster bonding in B₁₂ crystals as well as bonding between icosahedra situated in different planes are the most substantial, while the

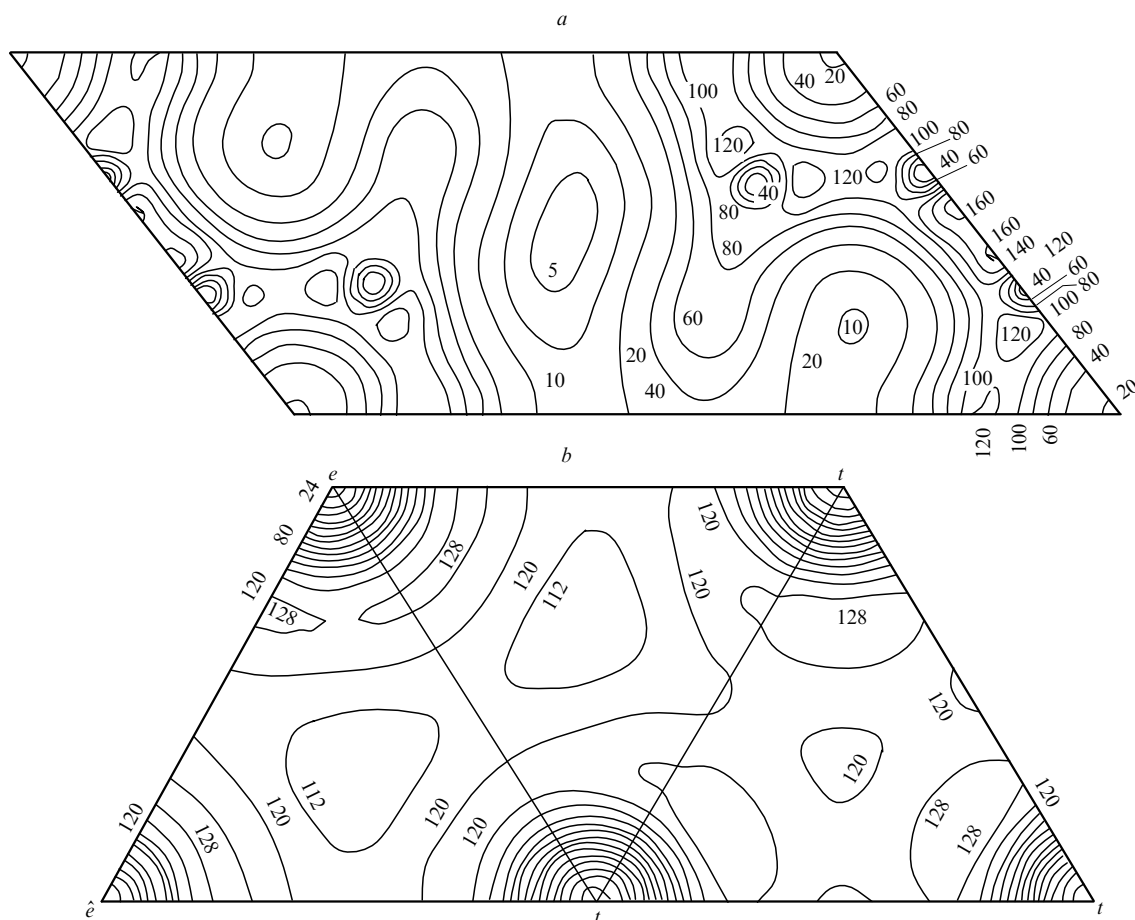


Figure 7. Charge density profiles inside α -B₁₂ crystal.

(a) Pattern vertices are at the centres of neighbouring icosahedra; (b) charge density in three faces of the B₁₂ icosahedron with boron atoms in t , e and $\bar{e}$ positions. Numbers at contours are charge density values in millielectrons per atomic unit.

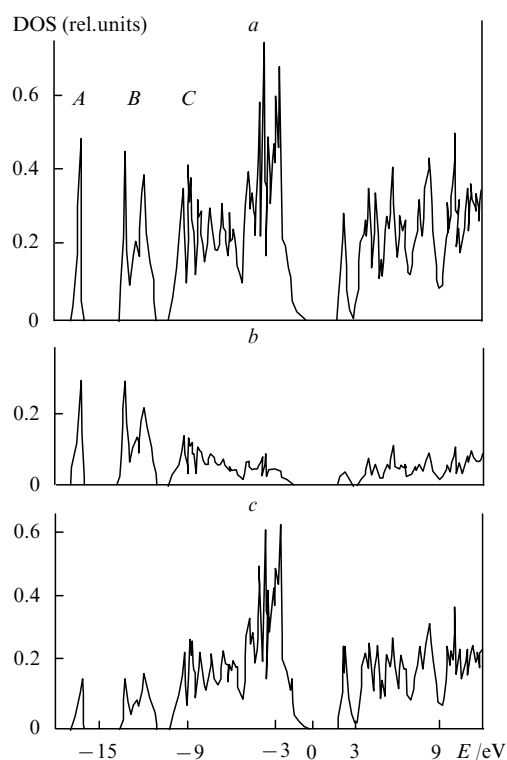
Table 1. Energy spectra parameters for α -B₁₂ and α -B₅₀.⁸⁶

Parameter	α -B ₁₂	α -B ₅₀
FG /eV		
indirect FG	1.70 ($Z \rightarrow I$)	—
direct FG	2.17 (I)	2.16 (I)
	4.12 (X)	3.20 (X)
	2.79 (Z)	3.95 (S)
	3.53 (A)	2.90 (Z)
	4.12 (D)	—
experiment ⁸³	1.19	—
calculations		
(indirect FG /eV)	1.43 (see ⁸⁵)	—
	1.70 (see ⁷⁹)	—
	2.40 (see ¹¹⁰)	—
Subband width ^a /eV		
C	10.00	10.67 (filled)
		1.37 (above E_F)
B	2.57	2.03
A	0.82	0.33

^a For subbands A – C , see Fig. 8.

bonds between clusters lying in the same plane are much weaker. Another electron band calculation of α -B₁₂ using the orthogonalised linear combination AO method (OLCAO),^{86,87} was done with the set of $1s, 2s, \dots, 3p$ orbitals.⁸⁶ The form of the dispersion function $E(\vec{k})$ allowed one to assign⁸⁶ α -B₁₂ to semiconductors with an indirect FG of 1.8 eV. Table 1 lists the corresponding experimental data along with the values of ΔE_g obtained in other calculation schemes. The observed differences between the calculated FG values are mostly the result of different correlation exchange formalism and different basis sets.

Figure 8 shows the total and local densities of states (TDOS and LDOS respectively) in α -B₁₂.⁸⁶ The ‘ A ’ band (with occupation

**Figure 8.** Total density (a) and local density of B 2s (b) and B 2p states (c) in α -B₁₂.⁸⁶

number, ON=8 e) is composed mainly of B 2s AOs and is separated from the ‘ B ’ and ‘ C ’ bands (ON=12 and 16 electrons, respectively) by a narrow (~ 0.5 eV) gap. The ‘ B ’ band has a mixed p – s -character, while the ‘ C ’ band corresponds mainly to boron 2p- AOs. The calculated optical characteristics of α -B₁₂⁸⁶ are in reasonable agreement with the experimental data,^{88,89} which makes it possible to reproduce the general shape of the optical absorption spectrum and to explain the positions of its major maxima.

Finally, the paper⁹⁰ aimed at the theoretical modelling of probable structural transformations of α -boron under high pressures (P), has to be mentioned. The model assumed that the kinetic energy (E_k) of the electron subsystem increases at the expense of its potential energy (E_p). This assumption is well known for condensed phases with covalent interactions, where substantial localisation of electron density on interatomic bonds is observed. Since E_p and E_k are proportional to $V^{-1/3}$ and $V^{-2/3}$ respectively (where V is a cell volume), an increase of pressure associated with a decrease in V , will probably result in a faster increase in E_k . So, it will lead to a more uniform distribution of the electron density and in a closer packing as a consequence. This tendency was confirmed in many experimental^{91–97} and theoretical^{98–103} solid state studies.

The analysis of this effect was based⁹⁰ on calculations of boron crystal total energy (E_{tot}) as a function of volume. The calculations were performed using a non-empirical pseudo-potential (PP) method in LDA approximation^{104–107} and the linearised MTO method (LMTO).¹⁰⁸

As possible boron allotropes, α -B₁₂, diamond-like, simple cubic (c), face-centred cubic (fcc), body-centred cubic (bcc), and hexagonal closely packed (hcp) structures were considered. Probable distortions of boron structure from bcc to body-centred tetragonal (bct) form were also taken into account.

The dependence of the total energy on volume [$E_{\text{tot}}(V)$] obtained in the LMTO calculations⁹⁰ is shown in Fig. 9. A similar correlation was found in PP calculations. Table 2 summarises the equilibrium volume, bulk modulus, and the corresponding minimum values $E_{\text{tot}}(V_0)$ from PP and LMTO calculations for all structures along with the experimental data.¹⁰⁹ These data demonstrate that α -B₁₂ is the most stable structure at normal pressures, whilst on a pressure increase (and volume decrease), a structural phase transition α -B₁₂–bct (at $P \sim 210$ GPa) should occur followed by a stabilisation of the bcc form (at $P \sim 360$ GPa).

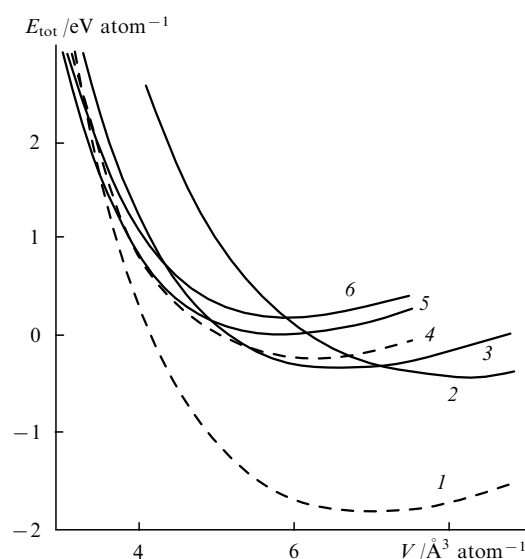
**Figure 9.** Total energy vs. volume for α -B₁₂ (1), boron with diamond structure (2), simple cubic (3), body-centred cubic (4), face-centred cubic (5), and hexagonal closely packed (6) boron sublattice. LMTO calculations.⁹⁰

Table 2. Equilibrium volume (V_0), bulk modulus (B_0), and total energy [$E_{\text{tot}}(V_0)$] for different boron crystalline structures (see text).

Structure	$V_0/\text{\AA}^3$		B_0/Mbar		$-E_{\text{tot}}/\text{eV atom}^{-1}$	
	PP	LMTO	PP	LMTO	PP	LMTO
Calculations						
$\alpha\text{-B}_{12}$	7.05	6.93	2.49	2.66	1.43	1.83
Diamond-like B	7.93	8.23	1.86	1.86	0.32	0.42
Simple cubic B	6.43	6.65	2.41	2.43	0.24	0.35
fcc	5.65	5.91	2.69	2.66	0.00	0.00
hcp	5.72	5.99	2.68	2.55	-0.19	-0.18
bcc	5.88	6.12	2.37	2.32	-0.38	-0.29
Experiment ¹⁰⁹						
	7.28		2.0		—	

This transitions should be accompanied by a weakening of certain localised covalent B—B bonds, a decrease in the forbidden zone, and a transition of bcc structure to a metallic-like state as observed in aluminium.¹¹⁰

Tetragonal $\alpha\text{-B}_{50}$. The crystal structure of $\alpha\text{-B}_{50}$ has been described.^{111–116} The tetragonal cell with the parameters $a = 8.75$, $c = 5.06$ Å includes 4 ideal icosahedra and 2 boron atoms [B(A)] with 4-fold coordination. Boron atoms composing icosahedra can be subdivided into 4 types [B(1)...B(4)] depending on their position relative to other B_{12} polyhedra and B(A) atoms (see Fig. 1b). Only one type of boron atom that does not belong to the icosahedron may be present.

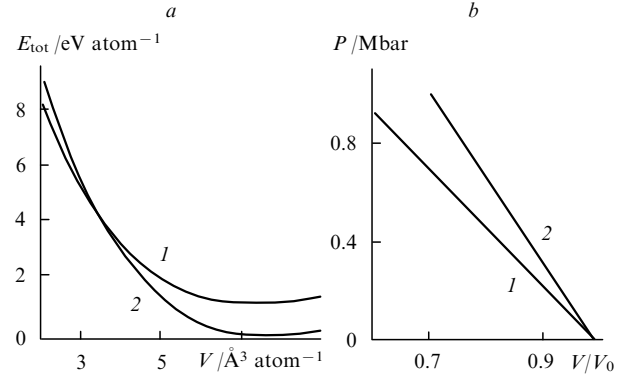
Quantum-chemical calculation of $\alpha\text{-B}_{50}$ by simple LCAO method⁷⁹ allowed one to describe a general structure of its electron energy spectrum. It includes partially filled valence band formed by boron $2s$ and $2p$ AOs, which determines metal-like properties of the tetragonal $\alpha\text{-B}_{50}$. This band is separated from the lowest unoccupied band by FG of ~ 1.43 eV. To fill the valence band during the corresponding transition from the tetragonal phase into the more stable semiconducting phase, 10 additional electrons per unit cell are needed. This explains a known tendency of $\alpha\text{-B}_{50}$ to form stable compounds with electron-rich p -elements (C, N).

To date the best of the most rigorous calculations of $\alpha\text{-B}_{50}$ was performed by OLCAO method.⁸⁶ Analysis of TDOS shapes for $\alpha\text{-B}_{50}$ demonstrated the metallic character of the phase with the FG of about 2.16 eV width lying above the Fermi level by 1.38 eV. The spectrum of the filled states consists of three main subbands with the occupation numbers of 8, 24, and 128 e, respectively. The main differences in EES parameters for $\alpha\text{-B}_{12}$ and $\alpha\text{-B}_{50}$ are clearly seen in Table 1. The decomposition of TDOS onto partial components [corresponding to atom types B(A), B(1)...B(4), see Fig. 1b] shows that the electronic states of B(A) and B(1) that form local bonding orbitals of the [B(A)B(1)₄] tetrahedron make the main contribution to the Fermi level (*i.e.* are responsible for the metal character of $\alpha\text{-B}_{50}$).

Analogies between atomic structures of $\alpha\text{-B}_{50}$ and fullerene C_{60} as well as electronic structures of $\alpha\text{-B}_{50}$ and $\text{YBa}_2\text{Cu}_3\text{O}_7$ were observed.⁸⁶

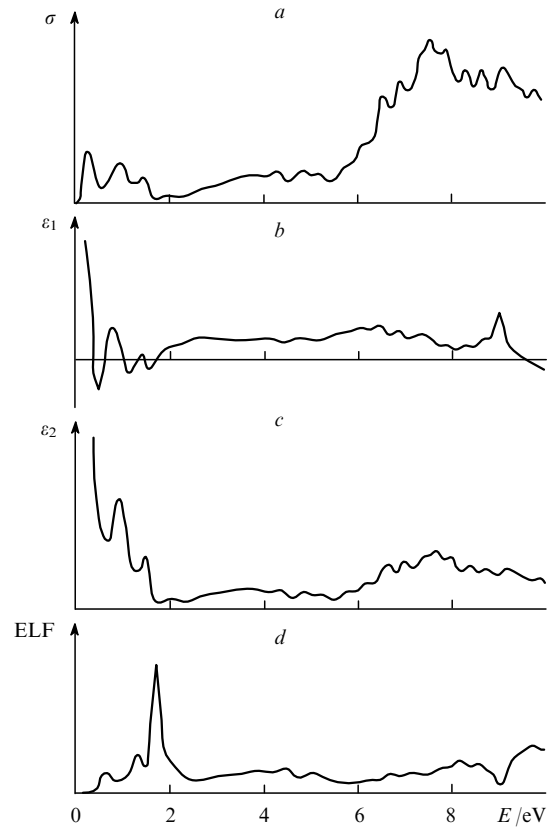
In the latter case, both $\alpha\text{-B}_{50}$ and the superconducting oxide possess a subband of hole states near the Fermi level separated from the higher virtual states by a semiconductor gap.^{117–119} The analogy allows one to suggest that $\alpha\text{-B}_{50}$ may exhibit superconductivity.⁸⁶

The relative instability of $\alpha\text{-B}_{50}$ may be explained by the presence of unfilled states between E_F and the bottom of the forbidden zone. The tetragonal $\alpha\text{-B}_{50}$ structure can be stabilised by doping with electron-rich nonmetals to form phases like $\text{B}_{48}\text{B}_2\text{C}_2$ or $\text{B}_{48}\text{B}_2\text{N}_2$ ^{120, 121} or with d/f -elements to form higher borides. Calculations of E_{tot} vs. volume dependence, estimates of

**Figure 10.** Total energy vs. volume (a) and pressure vs. volume (b) for $\alpha\text{-B}_{12}$ (1) and $\alpha\text{-B}_{50}$ (2), V_0 is the equilibrium volume.

V_0 , B_0 , and $P(V/V_0)$ for $\alpha\text{-B}_{50}$ showed that $B_0(\alpha\text{-B}_{50}) > B_0(\alpha\text{-B}_{12})$ (Fig. 10). This fact indicates higher hardness of the tetragonal phase. The $P(V/V_0)$ function indicates a higher thermodynamical stability of $\alpha\text{-B}_{50}$ (at 0 K), although a phase transition $\alpha\text{-B}_{50} \rightarrow \alpha\text{-B}_{12}$ is possible when the external pressure is increased up to ~ 360 GPa. This high pressures can result in substantial structural distortions of both phases and does not exclude a possibility of formation of alternative structural modifications,⁸⁶ similar to those discussed elsewhere.⁹⁰

Figure 11 shows the calculated optical characteristics of $\alpha\text{-B}_{50}$:⁸⁶ the interband absorption (σ), real (ϵ_1) and imaginary (ϵ_2) parts of dielectric functions, and energy loss function (ELF) in the range of 0–10 eV. The $\sigma(E)$ function contains peaks at the energies ~ 1.1 and 1.5 eV related to the transitions from the filled band to the unoccupied band near the Fermi level. The minimum

**Figure 11.** Changes of σ (a), ϵ_1 (b), ϵ_2 (c), and ELF (d) for $\alpha\text{-B}_{50}$ in the photon energy range 0–10 eV (for notations see text).

of $\sigma(E)$ in the region 2.0–5.5 eV corresponds to the forbidden zone in the energy spectrum. Above 5.5 eV, the absorption intensity increases abruptly (due to transitions to unoccupied states above the forbidden zone), and the structure of $\sigma(E)$ in this region becomes similar to that of α -B₁₂.⁹⁰

Rhombohedral β -B₁₀₅. The crystal structure of β -B₁₀₅ has been determined.^{122–125} The main building block of the structure is a B₈₄ polyhedron (Fig. 12) that includes a central icosahedron coordinated by 12 pentagonal pyramids B₆. The unit cell of β -B₁₀₅ contains 15 structurally non-equivalent positions occupied by boron atoms.

The complexity of the β -B₁₀₅ structure hampers strict non-empirical quantum chemistry calculations of its EES. Thus, the

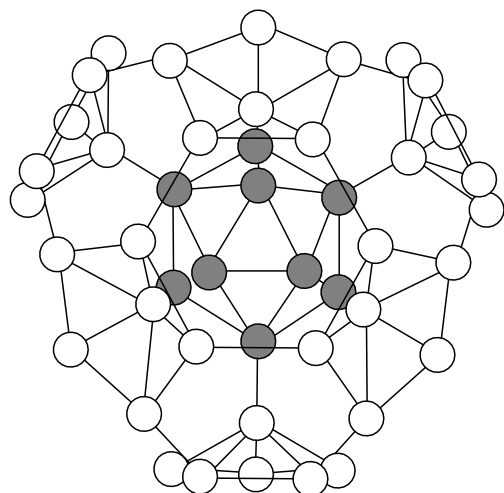


Figure 12. The structure of the central part of 84-atomic polyhedron, which is the principal building block in β -B₁₀₅ crystal lattice.

energy spectrum of β -B₁₀₅ was calculated only using a simplified LCAO approach under the two-centre approximation.⁷⁹ The TDOS histogram obtained (Fig. 13) exhibits fine structure. However, assignment of its peaks to structurally non-equivalent groups of boron atoms was not performed.⁷⁹ Complete filling of the valence band requires 320 electrons while unit cell contains only 315 e. Therefore, β -B₁₀₅, like α -B₅₀, should exhibit metal-like

properties. The width of the forbidden zone (in the region of unoccupied states) in β -B₁₀₅ is estimated as ~ 2.7 eV.

Numerous experimental data (see, for example, a review¹²⁶) demonstrate that filling of cell cavities in β -B₁₀₅ by transition metal atoms results in certain cases in the increase in microhardness of the phase and dramatically changes its conductivity.^{127–129}

It should be generally noted that experimental studies of β -B₁₀₅ [using XES,^{130–134} XPS,^{135,136} optical absorption,^{137–143} Raman spectroscopy,^{144–146} Auger electron spectroscopy (AES),¹³⁵ and ESR^{147–151}] lead to inconsistent conclusions as to its conductivity. For instance, according to optical absorption and XPS data,^{136,138–143} β -boron is a semiconductor with an indirect FG equal to 0.65–1.73 eV. However, according to ESR data,^{147–151} the forbidden zone of β -B₁₀₅ contains a system of ‘trap’ levels composed of different states of non-equivalent B atomic groups, which causes several types of jumping conductivity. An empirical scheme of β -B₁₀₅ band structure reflecting this feature has been proposed¹⁵² (Fig. 14). Werheit¹⁵³ confirmed and developed this model based on the recently obtained experimental results^{154–159} (mainly from visible, IR, and Raman spectra, conductivity measurements and magnetic parameters) both for pure and doped β -boron.

The correct interpretation of all experimental data on β -B₁₀₅ (see also Refs 160, 161) definitely requires further detailed calculations of its spectral fine features.

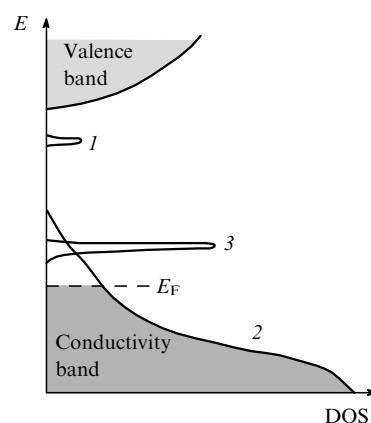


Figure 14. Energy bands scheme for the rhombohedral β -boron; (1–3) are states localised near the Fermi level determining possible types of jumping conductivity. Valence band and conductivity band dashed.

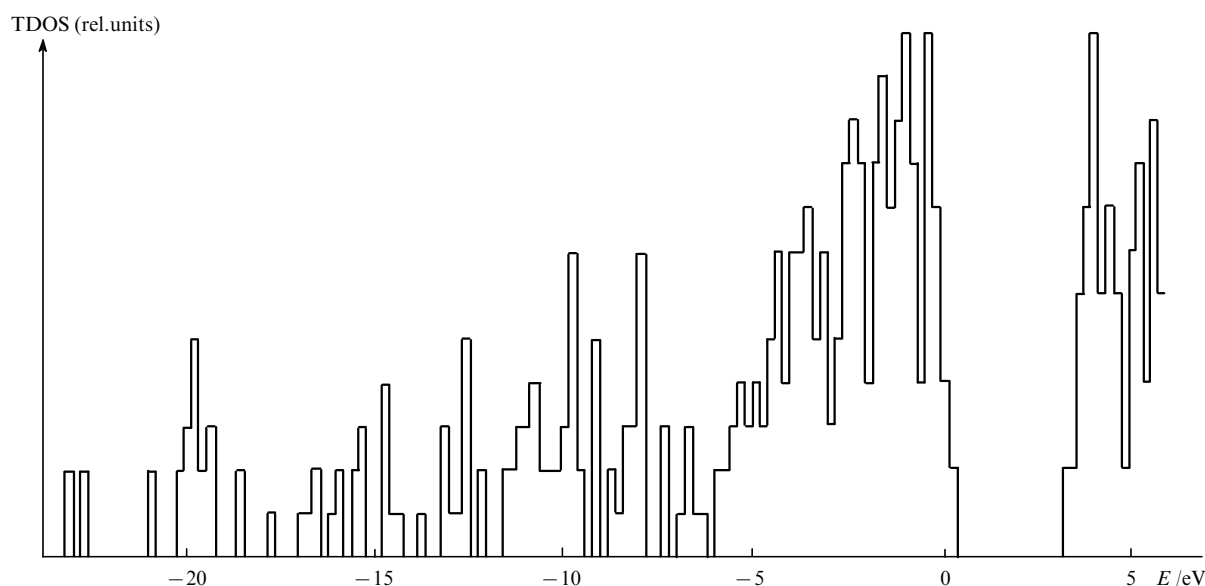


Figure 13. Total density of states of β -B₁₀₅. LCAO calculations.

2. Amorphous boron

The electronic factors that determine the relative instability of crystalline forms of boron are responsible for the existence of its amorphous state. Amorphous boron usually exists as films deposited on certain supports. Numerous studies were devoted to the formation conditions and the properties of amorphous boron^{2, 5, 25, 37–41} though most technological and scientific interest lies in its amorphous alloys with metals (like $M_{80}B_{20}$, *etc.*). In the experimental studies dedicated to amorphous boron (AB), the main attention has been paid to the investigation of the mechanism of its transition into the crystalline state.^{162–165} According to conductivity measurements, AB is an amorphous semiconductor.^{151, 166, 167} The structure of AB may be described as a conglomerate of atomic clusters composed of B_{12} polyhedra^{168–176} with a size in the range 2–5 nm.¹⁷⁷

Data on EES of AB are rather scarce and in most cases are based on XES.^{130–132, 177, 178} According to literature data,^{130, 177, 178} the boron K_{α} -spectrum in AB is similar to that of β - B_{105} except for a shoulder at 179 eV that is more intense for β -boron.

The combination of XES and extrinsic photoeffect quantum yield spectrum on a common scale allowed one to estimate a FG for AB as 1.2 ± 0.2 eV,¹³¹ which is in a reasonable agreement with the photoconductivity data (1.27 ± 0.05 eV¹⁷⁹) and estimations from measurements of high-temperature conductivity of AB films (~ 1.00 eV¹⁴²). The analogy of the optical properties of AB and β - B_{105} was also observed,¹⁶⁶ the study of optical absorption and photoeffect for AB gives indirect FG value equal to 0.56 ± 0.03 eV.

III. Boron carbides

Boron carbides (B_xC_y) exhibit very interesting properties.^{1, 7, 11, 15, 25, 28, 32–41, 180} Phase relations in B–C systems were investigated in much detail, and the existence of a number of individual phases as well as interstitial solid solutions (for example, of boron or carbon in $B_{12}C_3$, see^{37–39, 41}) was clearly demonstrated. According to recent data,^{38, 39, 41, 180–186} structures of carbides with lower carbon content (from 9 at.% to 20 at.%, *i.e.* from $B_{10}C$ to $B_{12}C_3$) are connected with the parent structures of solid boron. The main building blocks of these structures are B_{12} -like icosahedral clusters.

In a number of studies,^{187–189} the synthesis of carbon-rich carbides $BC_{3 \pm x}$ with layered graphite-like structure was reported. In addition to the phases mentioned above, numerous heterogeneous boron carbide phases ($B_{13}C_2 + C$), non-stoichiometric boron-carbon compounds $B_{1-x}C_x$,^{183–186, 190} and B_xC_y -based composites¹⁹¹ are also known. The electromagnetic,^{192–196} spectroscopic,^{197–199} and thermal²⁰⁰ properties of B_xC_y phases as well as their behaviour in reactions with metals,²⁰¹ oxides,²⁰² ferroalloys,²⁰³ *etc.* have been thoroughly investigated.

A phenomenological model of chemical bonding in boron carbides containing B_{12} polyhedra ($B_{13}C_2$, $B_{12}C_3$)¹⁸⁰ describes these polyhedra as electron-deficient systems with ‘delocalised’ covalent bonding. A possibility of different electronic configurations (sp^2 and sp^3) for carbon atoms is suggested. Using atomic-term energies for B and C, the heat of boron carbide formation and atomisation of boron and carbon, the degree of metallicity, covalency, and ionicity has been estimated to be 0.58, 0.93, and 0.35 respectively.¹⁸⁰ In fact, the qualitative character of these estimates cannot be a serious basis for the micro-level description (and, moreover, predictions) of the fundamental electronic properties of B_xC_y phases.

Three ordered phases, *viz.* $B_{13}C_2$, $B_{12}C_3$, and BC_3 , were the subject of several studies using advanced computational methods of quantum chemistry. Special attention has been paid to the calculation of EES parameters and to the problem of reliable determination of crystal structures. The relative stability of the possible icosahedra (B_{12} and $B_{11}C$) composing the $B_{13}C_2$ and $B_{12}C_3$ carbides is still under discussion. The composition of

triatomic ‘intercluster’ linking chains also remains obscure (the suggested variants are CBC, CCC, BBC).

Boron carbide $B_{13}C_2$. The structure of $B_{13}C_2$ is still a subject of lively discussions. $B_{11}C$ clusters and (BBC) chains were suggested as main building blocks of the structure.^{194, 195, 197} On the other hand, an alternative variant of B_{12} clusters and CBC chains (Fig. 15) was discussed^{204–206} on the basis of X-ray diffraction data. Experimental difference electron density maps were also obtained.^{204–206} Analysis of these maps lead to a conclusion that B(3)–C σ -bonds dominate within C–B(3)–C chains, between these chains and icosahedron [C–B(1)] and between atoms of the icosahedron [B(2)–B(2)].

A structural model^{203–207} was used for the band structure and cluster calculations of the electronic properties of $B_{13}C_2$.²⁰⁸ It was found that the dispersion $E(k)$ in all symmetrical directions of the

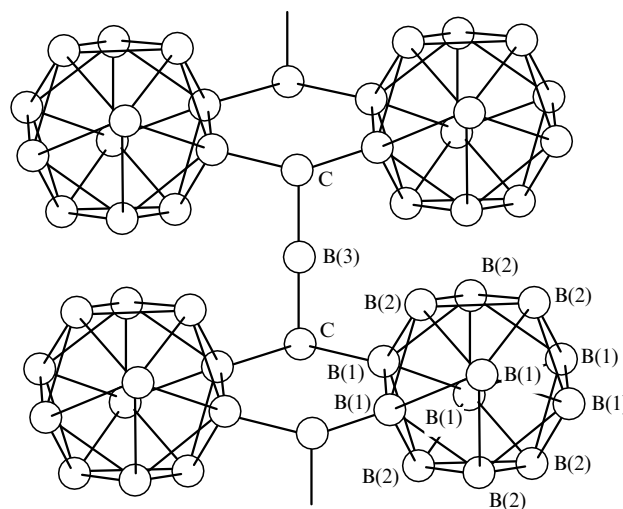


Figure 15. Structure of $B_{13}C_2$.²⁰⁴

Brillouin zone (BZ) does not exceed ~ 3 eV, the carbide VZ is filled only partially and is separated from the forbidden zone ($\Delta E_g \sim 4$ eV) by a subband of unfilled states. According to data,²⁰⁸ $B_{13}C_2$ should exhibit metal-like properties. It was concluded²⁰⁸ that the conductivity of the carbide phase will decrease as the content of carbon increases (in the row $B_{13}C_2 \rightarrow B_{12}C_3$, *i.e.* on filling of unoccupied upper region of the VZ). It agrees generally with an empirical interpretation of changes in conductivity of B_xC_y .²⁰⁹

Pseudomolecular calculations²¹⁰ with Born–Karman boundary conditions were performed in order to determine bond and charge state parameters for $B_{13}C_2$ (Table 3). It is clearly seen that bond populations in icosahedra are noticeably lower than for the ‘chain’ bonds. Relative charges on different atoms (B or C) are in accordance with their electronegativities. This conclusion also

Table 3. Bond populations (I) and effective charges (q) of atoms and groups of atoms in $B_{13}C_2$ phase.²¹⁰

Bond ^a	I / e	Atom ^a	q / e
B(1)–B(1)	0.50	B(1)	0.20
B(1)–B(2)	0.49	B(2)	–0.16
B(2)–B(2)	0.52	B(3)	0.81
B(3)–C	1.05	C	–0.57
B(1)–C	0.83	I ^b	0.33
		II ^c	–0.33

^a For atom notations, see Fig. 15. ^b I is a B_{12} icosahedron. ^c II is a CBC chain.

holds for atomic groups of the elements considered. The general tendency of charge density polarisation (in the direction $B \rightarrow C$) agrees with experimental data.^{204–206}

In the most rigorous non-empirical calculations of the energy band structure for $B_{13}C_2$,²¹¹ two alternative structures of the carbide $B_{12}(CBC)$ and $B_{11}C(BBC)$ were considered. For the latter, three possible arrangements of carbon atoms in the icosahedron and in the chain were taken into account.²¹² In two cases (α and γ), the carbon atoms occupied the terminal positions of the chain, and the ‘icosahedral’ carbon lay in the equatorial plane of the polyhedron near the chain carbon atom (α) or far from it (γ). The case β implies that a carbon atom is situated in the lowest vertex with no direct $C-C$ bonds.

The relative stabilities of the above structural types were compared based on their bonding energies (Table 4). The $B_{12}(CBC)$ form appeared to be the most stable. This conclusion is supported by comparison of the free energy values F ; for $B_{11}C(BBC)$, taking account of the number of possible configurations (α, β, γ) is given by a formula:

$$F[B_{11}C(BBC)] = -kT \ln \left[6 \exp \left(-\frac{15E_\alpha}{kT} \right) + 12 \exp \left(-\frac{15E_\beta}{kT} \right) + 6 \exp \left(-\frac{15E_\gamma}{kT} \right) \right],$$

and for $B_{12}(CBC)$, by

$$F[B_{12}(CBC)] = -15E[B_{12}(CBC)].$$

Bonding energy values (see Table 4) give $F[B_{12}(CBC)] - F[B_{11}C(BBC)] = -1.669$ eV per unit cell.

Along with the energetic characteristics, the lattice constants, the equilibrium cell volume, bond lengths, and bond angles were calculated.²¹¹ The result for the $B_{12}(CBC)$ structure are in the best

involves only four electrons. This fact may cause the instability of the carbide and opens broad prospects for variations of the carbon content (from 4 at.% to 26 at.% of C).^{213,214}

The first simplified band theory calculation of $B_{12}C_3$ [$B_{12}(CCC)$ structure] was accomplished⁷⁹ using a basis of the valence $2s, 2p$ AOs of boron and carbon; a crystal potential was approximated by superposition of the atomic potentials. The results of the calculation showed a typical semiconducting structure of the VZ including a FG of ~ 3.8 eV. Semi-quantitative estimates of the effective atomic charges gave a transfer of two electrons from the central (in the CCC chain) carbon atom to $C-B_{12}$ bonds.

The features of the band spectra for $B_{12}(CCC)$ and $B_{11}C(CBC)$ were compared using the so-called ‘universal form’ of matrix elements within the pseudopotential scheme.⁵⁶ Estimates of one-electron bonding energies in the icosahedra composing the structures mentioned demonstrated that the corresponding value for $B_{11}C$ polyhedron exceeds that for B_{12} by ~ 3 eV. This may be considered as a qualitative confirmation of the CBC preferable chain configuration in $B_{12}C_3$.

A pseudopotential method was used²⁰⁸ to compare three possible structural forms of $B_{12}C_3$. The following structures were analysed: (1) $B_{11}C(CBC)$, where B(1) atom was replaced by carbon (Fig. 15); (2) $B_{11}C(CBC)$, where B(2) atom was replaced, and (3) $B_{12}(CCC)$, where B(3) atom was replaced. The E_{tot} values (Table 5) point to the instability of (3). IR data²¹⁵ and $^{13}C, ^{11}B$ NMR spectra^{216,217} also indicate the most probable formation of CBC chains oriented along the [111] direction in the structure of $B_{12}C_3$.

The cohesion energy for $B_{12}C_3$ [structure (2)] was estimated by the non-empirical self-consistent pseudopotential method²¹⁸ together with the equilibrium value of the lattice parameter. Calculated data conformed with the experimental value with the accuracy of 0.5%.

The most stable structure for $B_{12}C_3$ has been modelled²¹⁹ by the cluster Hartree–Fock method. The structure of boron carbide was approximated by a $B_{12}C_3H_6$ molecule, hydrogen atoms being introduced to compensate the ‘cleaved’ bonds. The analysis of E_{tot} for clusters with different configurations of the intericosahedral chains lead to a conclusion that the formation of the $C-B-C$ chains is preferable as compared to the $C-C-C$ chains.

The most comprehensive of the reported calculations for $B_{12}C_3$ [$B_{11}C(CBC)$ configuration] has been performed²²⁰ with the basis set of 3580 plane waves for 32 points of the IPBZ. Parameters of the energy band structure, equilibrium lattice constants, the value of (indirect) FG (2.781 eV), and effective atomic charges have been determined. Comparison of the cohesion energies (E_{coh}) for $B_{11}C(CBC)$ and alternative $B_{12}(CCC)$ configuration indicates that the former is more probable.

‘Devolution’ of the electron density maps for the faces of $B_{11}C$ icosahedron allows one to trace the charge distribution therein (Fig.16). This analysis demonstrated that the character of $B-B$ and $B-C$ bonds is mostly covalent.

Table 4. Cohesion energy (E_{coh} /eV atom⁻¹) for different $B_{13}C_2$ structures and diamond.²¹¹

Structure ^a	E_{coh}	Structure ^a	E_{coh}
$B_{12}(CBC)$	7.1408	$B_{12}(BBC)$	6.9312
$B_{11}C(BBC)$		$B_{11}C(CBC)$	7.2592
α	7.0013	B_{12}	6.8402
β	6.9926	Diamond	8.3895
γ	6.9482		

^a For notations of $B_{11}C$ (BBC) $\alpha-\gamma$, see text.

agreement with experimental data.^{204–207}

Thus, rigorous quantum chemistry calculations of energies for different structural models proposed for $B_{13}C_2$ give a convincing argument for a $B_{12}(CBC)$ form and allow one to reject all alternative variants.^{194,195,197}

Boron carbide $B_{12}C_3$. General information on the properties and structural features of the $B_{12}C_3$ phase has been summarised.^{37,39,41}

One of the first studies devoted to the qualitative description of the nature of chemical bonding in $B_{12}C_3$ ⁵⁰ stated that bonding of terminal and central carbon atoms in the $C-C-C$ chain

Table 5. Energy positions of the valence zone (E_{VZ}), conductivity zone (E_{CZ}), value of the forbidden gap ΔE_g , charges (q) on atoms B(1), B(2) and on icosahedra (q_n), and total energy per unit cell (E_{tot}) for different $B_{12}C_3$ structures.²⁰⁸

Structure ^a	$-E_{VZ}/\text{eV}$	$-E_{CZ}/\text{eV}$	$\Delta E_g/\text{eV}$	$-E_{tot}/\text{eV}$	$q[B(1)]/e$	$q[B(2)]/e$	q_n/e
1	6.8	2.8	3.0	710.59	+0.12; +0.22	-0.22; -0.11	0.16
2	6.7	3.0	3.7	711.92	+0.22; +0.11	-0.12; -0.22	0.30
3	7.1	4.2	2.9	704.49	+0.16	-0.21	-0.33

^a For structures 1–3, see text.

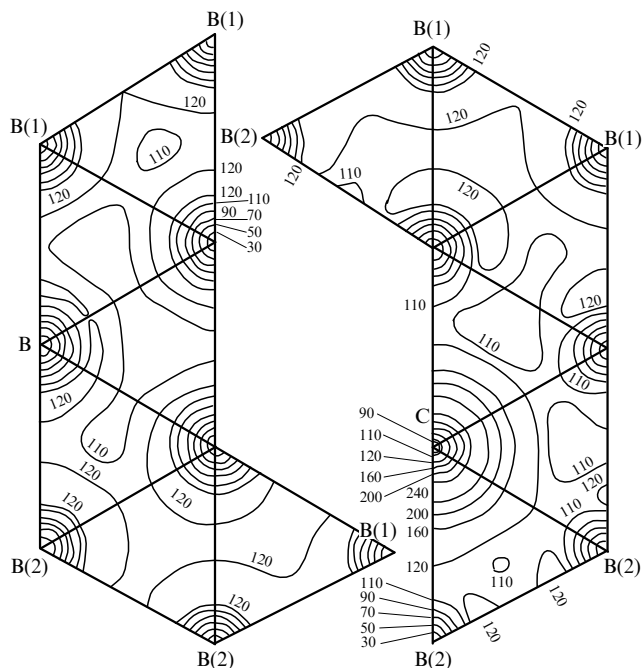


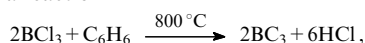
Figure 16. Charge density distribution in the faces of the $B_{11}C$ polyhedron in $B_{12}C_3$ [$B_{11}C(CBC)$ ordering type]. B(1) and B(2) atoms have, respectively, one and two carbon atoms in their closest environment. Numbers correspond to ρ values in 10^{-3} electrons per atomic unit.

The known²²⁰ value of E_{coh} for $B_{12}C_3$ was⁸⁵ used to calculate the heat of formation (ΔH) of the carbide according to the scheme:

$$\Delta H(B_{12}C_3) = 15E_{coh}(B_{12}C_3) - 3E_{coh}(C) - 12E_{coh}(B_{12}).$$

$E_{coh}(B_{12})$ was found in Ref. 85. The final calculated value of $\Delta H(B_{12}C_3)$ was 1.632 eV per unit cell, which is close to the experimental estimates of 1.795 and 1.940 eV per unit cell (see Refs 221 and 222, respectively). The somewhat smaller theoretical value of ΔH is probably due to the use of the valence approximation in this study.²²⁰

Boron carbide BC_3 . Synthesis of a layered boron carbide BC_3 via a reaction



has been reported.^{187–189}

It was pointed out, that partial B→C substitution in the graphite-like structure proceeds in a regular way with B_6 hexagons surrounding C_6 rings (Fig. 17). The density of the thus produced material is lower (since interatomic B–C distances are longer than C–C distances by ca. 10%) and its conductivity is higher than that of graphite.¹⁸⁸

The higher conductivity of the BC_3 may be caused by the lack of electrons in the carbide (as compared to graphite), which favours the appearance of a certain concentration of holes at Fermi level. In order to check this suggestion and to determine the nature of chemical bonding in BC_3 , a number of quantum-chemical calculations were performed.^{188, 223–225} According to estimates using the Hückel method,¹⁸⁸ the value of the forbidden gap in BC_3 is close to 1.8 eV and the Fermi level is located near the bottom of the π -band.

More rigorous *ab initio* calculations²²⁴ were performed using the pseudopotential LCAO method with a basis set of *s*- and *p*-AOs.²²⁶ Since interlayer separation in BC_3 (3.35 Å) is substantially larger than bond distances in the layer, calculations for a single layer of the carbide structure were carried out as the first step. Comparison of the electron density distribution in BC_3 monolayers (Fig. 18c) and graphite (Fig. 19) leads to a conclusion that the lesser electron density is concentrated on boron

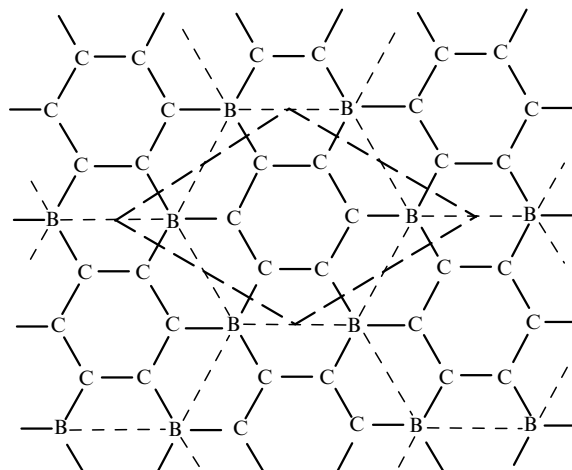


Figure 17. Structure of layered BC_3 (unit cell is shown).

atoms. However, electron distribution within C_6 rings is rather unperturbed, since the C–C interatomic distances in graphite and BC_3 are close.

The distribution of the density of states (DOS) for BC_3 single layers is shown in Fig. 18 and for graphite (Fig. 19). There is a FG between filled and unfilled states with the value of indirect transition ~ 0.66 eV. Account for interlayer interactions²²⁴ (with AA and AB possible relative orientations of neighbouring layers) results in a disappearance of the FG; the material acquires the properties of a metal with higher conductivity for the AA packing.

The conductivity of BC_3 carbide, therefore, is defined by interlayer interactions.²²⁴ However, the energy of these interactions is relatively small (according to some estimates,²²⁴ not higher

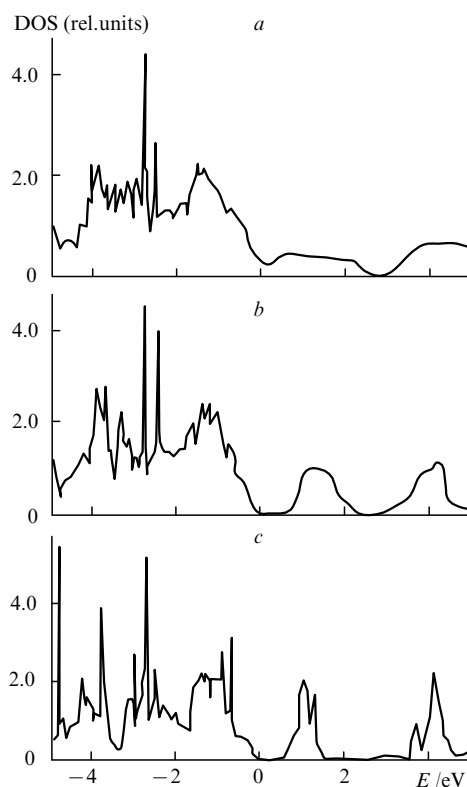


Figure 18. Density of states in BC_3 with (a) AA layers arrangement, (b) AB layers arrangement, (c) single layer.²²⁴

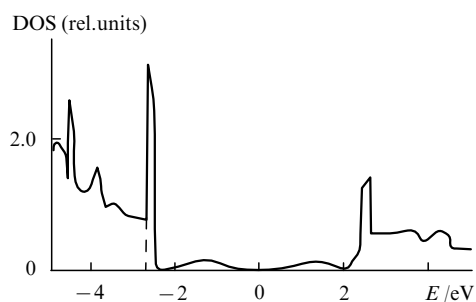


Figure 19. Density of states in graphite.²²⁴

than ~ 0.1 eV), although the total cohesion energy is about 7.8 eV.

The detailed analysis of changes in composition of states near the Fermi level for BC_3 compared to graphite was done²²⁵ using energy band calculations for single layers of graphite and BC_3 (Fig. 20). The analysis of the energy band distribution shows that the former σ -like bands are rather remote from the Fermi level and cannot take part in conductivity processes. However in the carbide the Fermi level (situated lower due to a decrease in general electron concentration) intersects the σ -band in the Γ point.

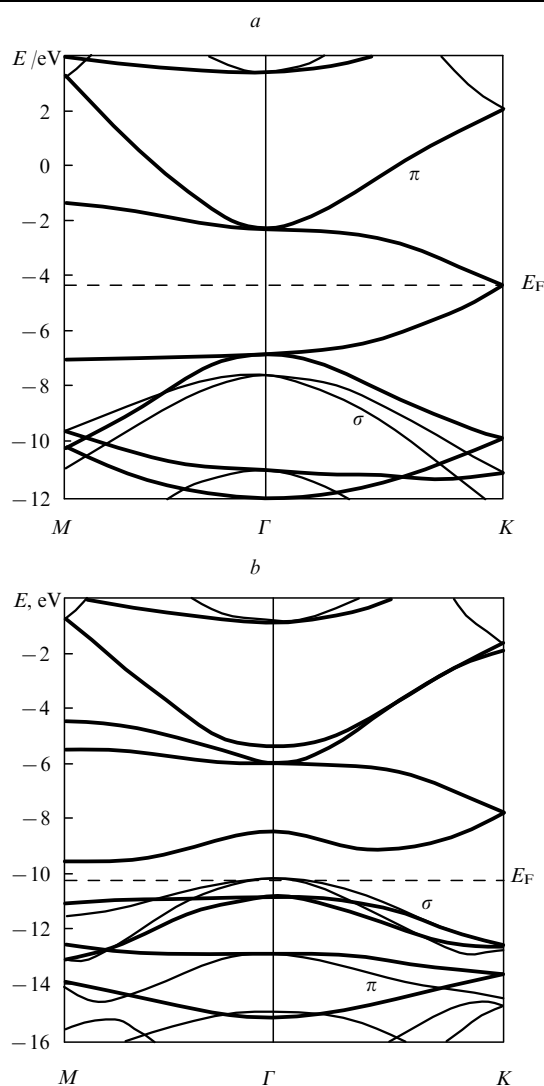


Figure 20. Energy band dispersion for single layers of (a) graphite and (b) BC_3 . The states with σ - and π - symmetry are marked, upper numbers denote a degeneracy.²²⁵

These bonds, along with π -like states, govern the conductivity properties of BC_3 (hole conductivity).

The above considerations were applied to a description of the electronic properties of boron carbides with a definite stoichiometry. However, along with such phases, a number of solid solutions (SS) with a variable composition are formed.

Recently,²²⁷ model calculations of electronic and structural parameters for one of these solid solutions, B_xC_{1-x} , with graphite-like structure have been carried out using the pseudopotential method under a local electron density approximation.²²⁷

It should be noted that the layered boron-carbon SS are usually prepared as films.¹⁸⁹ SS with a boron content less than 4% (intercalated graphites) can also be attributed to this type.²²⁸

The main goal of a study (Ref. 227) was to determine the most probable type of ordering for boron atoms in the graphite lattice. To this end, the total energy values for ordered and disordered structures of B_xC_{1-x} were compared. It was pointed out that intercluster interactions promote segregation of boron atoms and long-order formation in the case of SS with low boron content ($x \leq 0.25$). It was suggested²²⁷ that the increase in boron content should violate the ordered atomic arrangement with a transformation of the initial graphite-like crystal structure. This effect is primarily caused by the substantial difference in the atomic radii of boron and carbon.²²⁷

IV. Boron nitrides

Crystalline boron nitride BN, due to its unique properties and exceptional technological importance,^{15, 20, 26, 28–34, 36} is one of the best studied compounds of boron with p -elements. There are three known structural modifications of BN: hexagonal (graphite-like h-BN), cubic (sphalerite-like c-BN), and wurtzite-like (w-BN). The latter can be prepared from the h-BN as a result of a phase transition under high temperature/pressure treatment.

Synthetic methods, crystal structures, conditions of phase transitions (including the influence of lattice defects, admixtures, etc.) for boron nitrides were discussed in detail.^{26, 229–237}

Extensive experimental data obtained using XES, AES, XPS, absorption spectroscopy^{238–244} allow one to determine general features of EES of boron nitrides. The anisotropy of band dispersion for the layered BN was investigated²⁴³ using the polarised XES technique. This effect was also discussed in studies of Compton profiles in h-BN²⁴⁵ and of the electron inelastic scattering.²⁴⁶

Infrared and VIS-UV spectroscopies are widely used for characterisation of dielectric properties of nitrides.^{247–257} Their detailed comparison with the results of quantum chemistry calculations published before 1987 has been made.²⁵⁸ Electron energy loss spectroscopy has been used^{259–262} in order to obtain the EES parameters. The luminescence properties of BN were considered in Refs 263–267.

Theoretical studies of the fundamental properties of BN are also rather extensive. The first band theory calculation of the c-BN, which is a semiconductor of III–V type, in simplified TB approximation was performed in 1952.²⁶⁸ Since then, theoretical calculations of EES and many other properties have been carried out using almost all of the known band and cluster schemes for h-BN,^{269–286} c-BN,^{287–325} and w-BN.^{325–332}

Without going into discussion of the results of theoretical studies and some inconsistencies between the particular results (unavoidable because of different computational schemes, basis sets, potential parameters, etc.), we shall consider general electronic properties for all three modifications of BN calculated within the same approaches.^{324, 325}

The results of OLCAO band structure calculations for h-BN and w-BN are shown in Fig. 21a,b. Low energy bands of h-BN are composed mainly of $(\text{N}, \text{B})2s$ -states separated from the main hybrid $(\text{N}p-\text{B})2p$ band by an energy gap. The band structures for c-BN and w-BN are similar (Fig. 21c). Principal differences in the electronic structure parameters for the nitrides are clearly seen

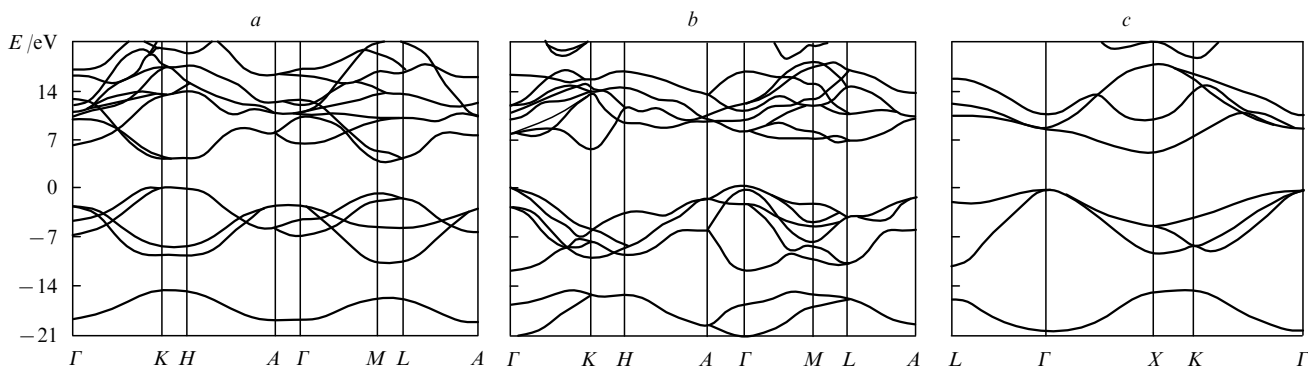


Figure 21. Energy bands of (a) h-BN, (b) w-BN, and (c) c-BN.

from Table 6. For the layered nitride, energy dispersion $E(\vec{k})$ along the direction k_z is relatively small. All BN modifications have indirect FG. For h-BN, the width of the VZ is minimum; in c-BN and w-BN it has comparable values due to a similarity of their atomic environments. This points to the local character of interatomic interactions that have a heteropolar nature in boron nitrides, determined, for instance, by B→N charge transfer (Table 6).

Recently, greater attention was paid to studies of EES in boron nitride crystals containing various structural defects. Investigations of complex systems (ceramics, composite materials based on boron nitrides, *etc.*) at the micro level will probably result in a substantial progress in the nearest future. However,

only a few studies have been performed in this field to date. The most interesting results are the following.

Studies of h-BN films^{326–329,331} (promising as inhibitory dielectric films and X-ray membranes) revealed a substantial dependence of their optical properties on stoichiometry (B/N ratio). To explain this fact, calculations were performed³³⁰ using TB approximation. A two-dimensional graphite-like structure was used as a model; variations in the composition of $\text{h-B}_x\text{N}_y$ (with assumption of random B→N substitution) were taken into account in coherent potential approximation.³³¹

The distribution of the π -type states indicates the absence of the FG in contrast to the experimental data³²⁹ that give decrease of the ΔE_g for h-BN from 5.0 to 2.5 eV when the B/N ratio changes from 1 to 5.1.

Accounting for a partial ordering of atomic configurations leads to appearance of the FG (Fig. 22) linked with the emerging of additional subband of the boron p-states, whose width is proportional to B/N ratio.³³⁰ Therefore, thin films of $\text{h-B}_x\text{N}_y$ should exhibit regular spatial distribution of the atomic components similar to that in the crystalline h-BN.

Table 6. Electronic and optical characteristics of boron nitrides.³²⁵

Parameter	h-BN	c-BN	w-BN
FG /eV			
indirect	4.07 ($H \rightarrow M$)	5.18 ($G \rightarrow X$)	5.81 ($G \rightarrow X$)
direct	8.9 (G)	8.7 (G)	8.0 (G)
	4.6 (M)	10.3 (X)	9.3 (X)
	5.6 (L)	12.4 (L)	10.7 (L)
	10.5 (A)	11.8 (K)	10.6 (A)
	4.2 (H)	—	12.8 (H)
	4.5 (K)	—	11.7 (K)
Band widths /eV			
upper VZ	10.40	10.94	11.76
gap between VZs	4.42	3.28	2.93
lower VZ	4.02	6.92	6.28
Effective charges on atoms /e			
B	2.70	2.80	2.99
N	5.30	5.20	5.01
Total energy /a.u. per molecule			
	−12.7638	−12.7123	−12.7011
Pressure of electron-nucleus system/MBar			
	3.35	3.70	3.90
Dielectric constant			
$\epsilon(0)$	3.61	3.86	4.17
$\epsilon_i(0)$	4.32	—	4.16
$\epsilon_{11}(0)$	2.21	—	4.18
Main plasmon peaks /eV			
	11.6	27.3	26.4
	23.7	32.5	32.0
	36.3	38.5	

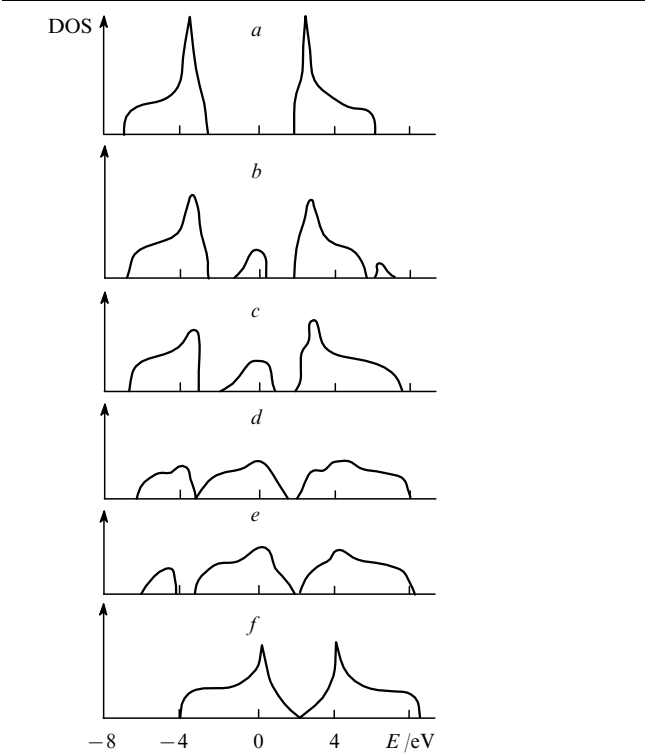


Figure 22. π -DOS distribution in the 2D-layer of boron nitride.³³⁰ The B/N ratio is 1 (a), 1.25 (b), 2 (c), 5 (d), 8 (e); (f) pure boron.

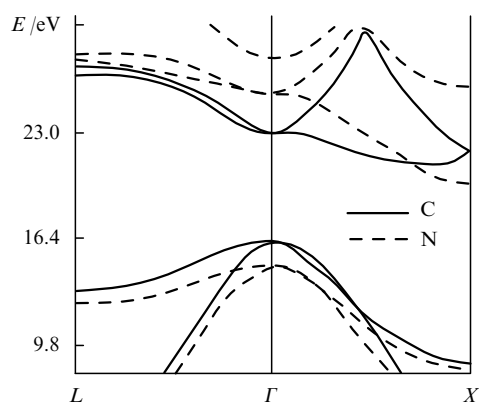


Figure 23. Energy bands of the heterogeneous phase system (110) diamond – boron nitride.

The features of the energy states, typical of the heterogenous system diamond/(boron nitride), have been analysed using the linearised method of augmented plane waves (LAPW).³³² A supercell that models the atomic geometry of the interface region including N/N layers ($N = 1; 3; 5$) of the C/BN (100) plane was used. It was found that energies of the internal layers and atomic charges for the central layer of each component become close to the corresponding values for the ideal C and BN crystals already for $N=3$. Band distribution near the Fermi level for the 5/5 layered system is shown in Fig. 23. It should be noted that, though the bottom of the conductivity zone is composed of BN bands (a gap between zones at the X point is about 0.7 eV), the top of the VZ relates to the ‘diamond’ states. The magnitude of the gap between zones is about 1.42 eV.

In Ref. 333, the method of an effective Hamiltonian^{334,335} (in Del Re parametrisation³³⁶) has been used as a theoretical basis for optimisation of the carbamide technology for h-BN preparation. In particular, carbamide $(\text{NH}_2)_2\text{CO}$ (1) was replaced in the technological process by cyanuric acid $\text{H}_3\text{C}_3\text{N}_3\text{O}_3$ (2) or melamine $(\text{NH}_2)_3\text{C}_3\text{N}_3$ (3). Atomic charges and energies of bonding states for the molecules (1)–(3) as well as for orthoboric acid and boric anhydride were estimated.³³³

Taking into account the electronic structure of the initial reagents and reaction products, it was pointed out³³³ that formation of h-BN in the interaction of carbamide, cyanuric acid, and melamine with H_3BO_3 may be considered as electrophilic substitution. In this mechanism, the boron and carbon atoms in H_3BO_3 , boric anhydride, and initial compounds 1–3 may be ranged in the order of decreasing activity towards orthoboric acid: $(\text{NH}_2)_3\text{C}_3\text{N}_3 > \text{H}_3\text{C}_3\text{N}_3\text{O}_3 > (\text{NH}_2)_2\text{CO}$. This has lead to a conclusion³³³ that the replacement of $(\text{NH}_2)_2\text{CO}$ by melamine in the multi-stage carbamide technology provides (due to its higher activity) a decrease in a number of stages. Replacement of carbamide by cyanuric acid results in a decrease in NH_3 output, *i.e.* in the increase of the environmental safety of the process.

V. Boron carbonitrides

Synthesis of a series of layered SS based on graphite and h-BN^{188,337,338} led to studies of their electronic spectra. Theoretical modelling of atomic ordering character in these systems was also carried out.^{339–341}

The electronic structure of a cluster composed of three hexagons of the h-BN single layer, where a central nitrogen atom is replaced by C, was calculated³³⁹ using the Gaussian orbitals LCAO (GO LCAO) method.³⁴² It was assumed that the carbon atom is situated 0.76 Å above the h-BN plane. Using the value of the constant of hyperfine interaction with ^{13}C nucleus (~ 1.8 Gs), it was possible to qualitatively explain the ESR splitting in a boron nitride enriched by carbon.^{343,344}

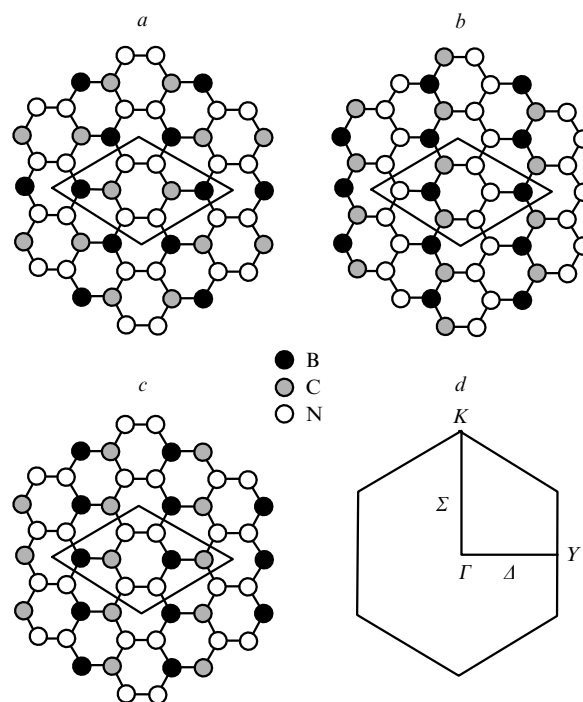


Figure 24. Models of atom ordering in boron carbonitride single layer (*a–c*) and Brillouin zone used for BC_2N calculations (*d*). Atomic ordering type: (*a*) *I*; (*b*) *II*; (*c*) *III*. Unit cell boundaries are shown.

Boron carbonitride BC_2N was considered as a two-dimensional crystal, and Extended Hückel (EH) band calculations of the BC_2N single layers were accomplished for three different atomic arrangements of the atomic in 8-atomic planar unit cell (Fig. 24).³⁴⁰ Interlayer interactions were not considered. It was found that the conductivity properties of the system depend strongly on the ordering type. For instance, the energy diagram for π -like band of BC_2N with the structure *I* (see Fig. 24 *a*) does not contain a forbidden gap, but for the ordered structures *II* and *III* (Fig. 24 *b,c*) ΔE_g is equal to ~ 1.8 and 2.9 eV, respectively. According to photoemission data and conductivity experiments,³⁴¹ the SS of BC_2N exhibits the metallic properties; therefore, the structure *I* was considered as the most probable for the BC_2N .³⁴⁰

The problem of atomic ordering and its influence on the electronic properties of BC_2N were also analysed using the pseudopotential method.³⁴¹ The same three models of structural ordering in the single layer were discussed (Fig. 24 *a–c*). According to the values of the adhesion and chemical bonding energies (Table 7), form *II* should be the most stable. According to the FG values obtained (Table 7), the phase *I* should exhibit the metallic properties, while the phases *II* and *III* are semiconductors (Fig. 25). It is noteworthy that the two-dimensional structural model (neglecting interlayer interactions) can substantially affect

Table 7. Chemical bonding energies (E_b), cohesion energies (E_{coh}), and forbidden gap values (ΔE_g) for boron carbonitride BC_2N with different structures of single layers.³⁴¹

Structure ^a	E_b	E_{coh}	$\Delta E_g/\text{eV}$
	eV per molecule		
<i>I</i>	23.7	20.0	—
<i>II</i>	24.7	21.2	1.6
<i>III</i>	23.7	18.5	0.5

^a see Fig. 24

^a see Fig. 24

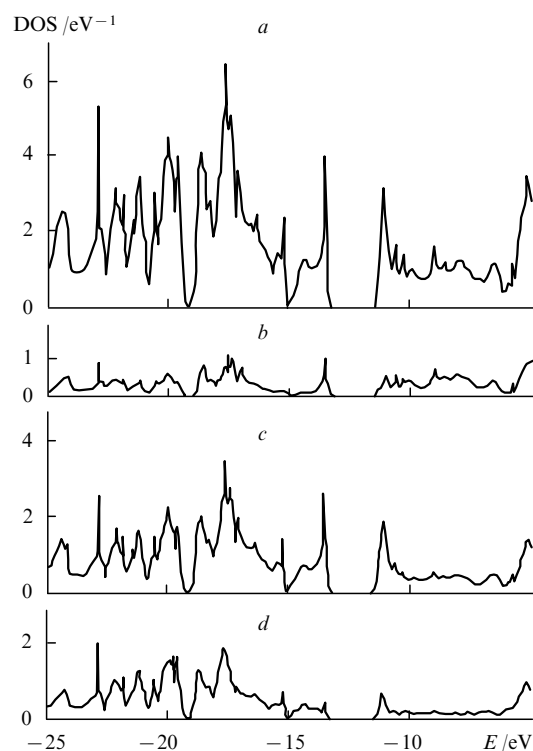


Figure 25. Total (a) and partial (b–d) density of states in BC_2N for the atomic ordering model II (see Fig. 24). Partial densities of states: (b) B; (c) C; (d) N.

the results of calculations. It was demonstrated,^{224, 307} that the interlayer interactions (in the *c* direction for h-BN and BC_3) increase the energy dispersion of π -bands which determine the conductivity properties of solid solutions. Further calculations that will take it into consideration are therefore required for a reliable theoretical description of conductivity.

VI. Nanostructures based on boron, boron carbides, and boron nitrides

The term ‘nanostructure materials’ usually refers to metastable cluster structures, *viz.*, nanospheres, nanoclusters, nanotubes. Rapid development of chemistry and technology of nanostructure materials is stimulated by a search for new substances without analogues in nature possessing unique topological, superconducting, catalytic and other properties.^{345–349} Most progress in the field recently is related to the synthesis and studies of carbon nanospheres, fullerenes.^{348, 350–356}

In the first attempt to prove theoretically the existence of polyhedral carbon C_n or hydrocarbon C_mH_m clusters, the Hückel model of the π -electron system has been used.³⁵⁷ MOs and resonance energies for the unsaturated carbododecahedron C_{20} and carbo-*s*-icosahedron C_{60} were calculated. Later, features of the electronic structures of buckminsterfullerene C_{60} , its isomers, and higher fullerenes were discussed in numerous publications;^{358–370} their structure and properties were extensively studied theoretically (see review 371). For spheroid fullerenes with a higher number of carbon atoms C_n ($n > 78$, giant fullerenes) a series of rather complicated structures were proposed (barrellenes, capsullenes, torrenes, *etc.*).^{372–375} The properties of cylindrical carbon macromolecules (tubulenes) and thread-like crystals formed on the base of the nanotubes have been discussed.^{376–378}

Recently, along with development of the technology for the preparation of new nanomaterials, a noticeable progress was achieved in the quantum chemistry of nanostructures formed in part on the basis of boron and/or its compounds with non-metals.

Direct modifications of the properties (including superconductivity) of the solid fullerenes C_n were carried out by including doping components into their structures, for instance, alkali metals, which act as electron donors.^{364, 379–382} An opposite effect (doping fullerenes with holes) may be achieved by partial substitution $\text{B} \rightarrow \text{C}$,³⁸³ or by an inclusion of halogen admixtures.³⁸⁴

The role of boron as a hole donor in the formation of the electronic properties of crystalline BC_{59} was examined by non-empirical band theory.³⁸⁵ Calculations of equilibrium lattice parameters (a_0) demonstrated that the $\text{B} \rightarrow \text{C}$ substitution results in a contraction of the BC_{59} polyhedron (as compared to the C_{60}) and a decrease in a_0 from 14.2 Å for C_{60} (see Ref. 386) to 13.5 Å for BC_{59} . DOS distributions in the valence zone region for C_{60} ³⁸⁰ and BC_{59} are similar. The only difference consists in an additional partially filled peak near the Fermi level (Fig. 26a) composed of the boron states with the admixtures of the π -type C $2p$ states of the neighbouring carbon atoms. The formation of these states (similar to the formation of the acceptor levels in a usual semiconductor) are clearly seen in the map of total charge density (Fig. 26b). Therefore, the result of the inclusion of boron into the solid-state C_{60} will be that fullerene will acquire more metallic character due to an appearance of dopant acceptor states in its valence spectrum. Estimates made of the energy²⁸⁵ showed that the above mentioned process is exothermic; the most probable product of the synthesis is a mixed C_{60}/BC_{59} fullerene.

The $\text{B} \rightarrow \text{C}$ substitution leads to a decrease in the electron concentration (per C_{60} molecule), BC_{59} MO system has an open electron shell. The increase in electron deficiency as the boron content increases will create progressive difficulties in the preparation of boron-rich fullerenes $\text{B}_x\text{C}_{60-x}$.

The electronic properties of mixed polyhedral clusters $\text{B}_n\text{C}_m\text{N}_k$ were discussed in a number of papers.^{387–396} Heats of formation of B_2C_{58} , C_{58}N_2 , BC_{58}N , $\text{B}_{24}\text{C}_{12}\text{N}_{25}$, and $\text{B}_{30}\text{N}_{30}$ were calculated and used for a discussion of stabilities of these molecules relative to C_{60} .³⁸⁷

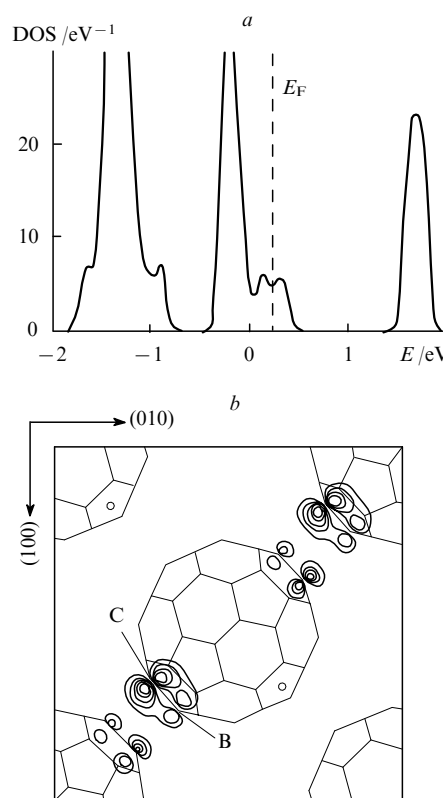


Figure 26. Total density of states for BC_{59} (a) and isoelectronic contours of charge density in the energy range $E_F - 0.1$ eV (b).

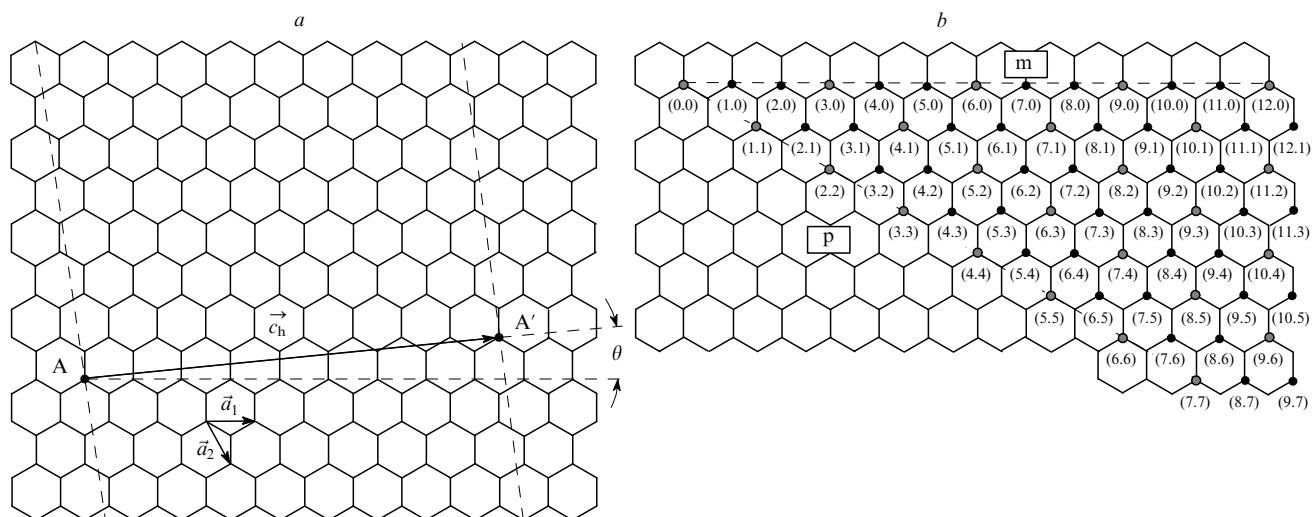


Figure 27. Illustration of the $\vec{c}_h$ vector selection that defines diameter and chirality of nanotubes formed by rolling single layers (point A conforms with A') (a) and possible vectors for chiral graphite nanotubes (b); m is metallic character of the nanotube, p is a semiconducting character.⁴⁰¹

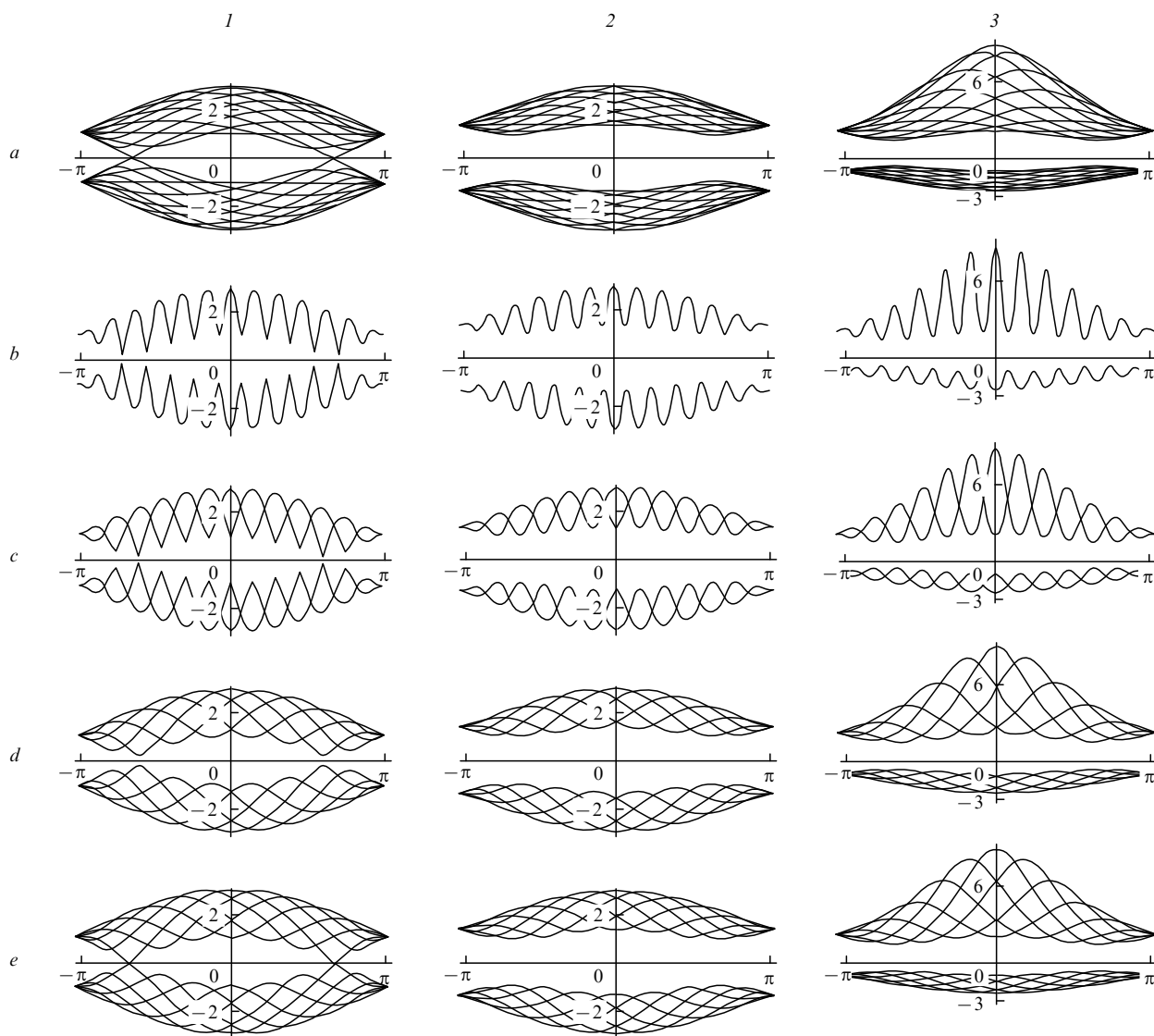


Figure 28. Energy bands for carbon (1) and BN (2,3) nanotubes with structural indexes (n,m) ; (n,m) : (a) (12,0); (b) (12,1); (c) (12,2); (d) (6,5); (e) (6,6); (1,2) Hückel calculations; (3) EHM calculations.

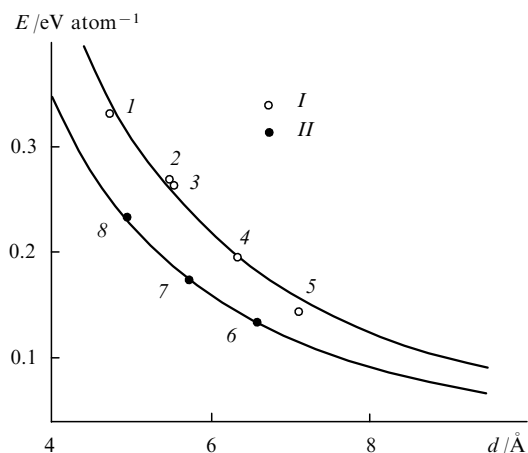


Figure 29. Deformation energies for nanotubes based on BC_3 (I) and graphite (II). (n,m) : (1), (6,0); (2), (7,0); (3), (4,4); (4), (8,0); (5), (9,0); (6), (4,0); (7), (2,2); (8), (3,0).

Taking into account the isoelectronic nature of a BH unit and the C atom, the existence of BH-formed nanospheres, which may be structural analogues of C_{60} , was predicted.³⁹⁷ For the synthesis of these species, laser ablation of layered graphite-like borides of alkali-earth metals in hydrogen atmosphere was suggested. It is noteworthy that the idea of the synthesis of stable boron-carbon clusters comes from the early works of Longuet-Higgins and Roberts,⁴⁹ in which the so-called ‘ $n+1$ ’ rule was proposed on the basis of MO theory. This rule gives electron concentrations of

Table 8. Cohesion energies for clusters based on BH and C .³⁸⁹

Cluster	$-E_{\text{coh}}/\text{eV}$	Cluster	$-E_{\text{coh}}/\text{eV}$
$\text{B}_{12}\text{H}_{12}$	9.37	$\text{B}_{12}\text{H}_{12}^{2-}$	9.98
$\text{B}_{32}\text{H}_{32}$	9.29	$\text{B}_{32}\text{H}_{32}^{2-}$	9.44
$\text{B}_{60}\text{H}_{60}$	8.82	$\text{B}_{60}\text{H}_{60}^{2-}$	8.86
C_{60}	8.50		

stable borohydrides with composition $\text{B}_n\text{H}_n^{2-}$ as in systems with close electron shells.

In order to examine the validity of the hypothesis proposed (cf. Ref. 397), the relative stability of $(\text{BH})_{60}$, an analogue of C_{60} , as well as those of $(\text{BH})_{32}$, $(\text{BH})_{12}$, and some other homologues, were estimated using local electron density functional theory.³⁹⁸ The analysis shows that borohydride nanocomplexes are more stable in ionic form. Their stability also increases as the average cross-section radius of the group decreases (Table 8).

Along with nanospheres, nanotubes, i.e. coaxially oriented fibres forming needle-like crystals, also attract considerable attention due to their unusual mechanical properties and conductivity.

These systems can be considered theoretically as a set of nanotubes (NT) with diameter of several nanometers. Each NT is formed by rolling up the corresponding planar atomic net and is characterised by a diameter and by the type of helicoidal ordering (chirality). If an NT is designed in this way, its diameter (d) and chirality may be described by a vector $\vec{c}_h = n\vec{a}_1 + m\vec{a}_2$ [the so-called (n,m) -NT] (Fig. 27). Then

$$d = \frac{|\vec{c}_h|}{\pi} = a \frac{[3(n^2 + m^2 + nm)]^{1/2}}{\pi},$$

where a is a bond distance in the planar network.

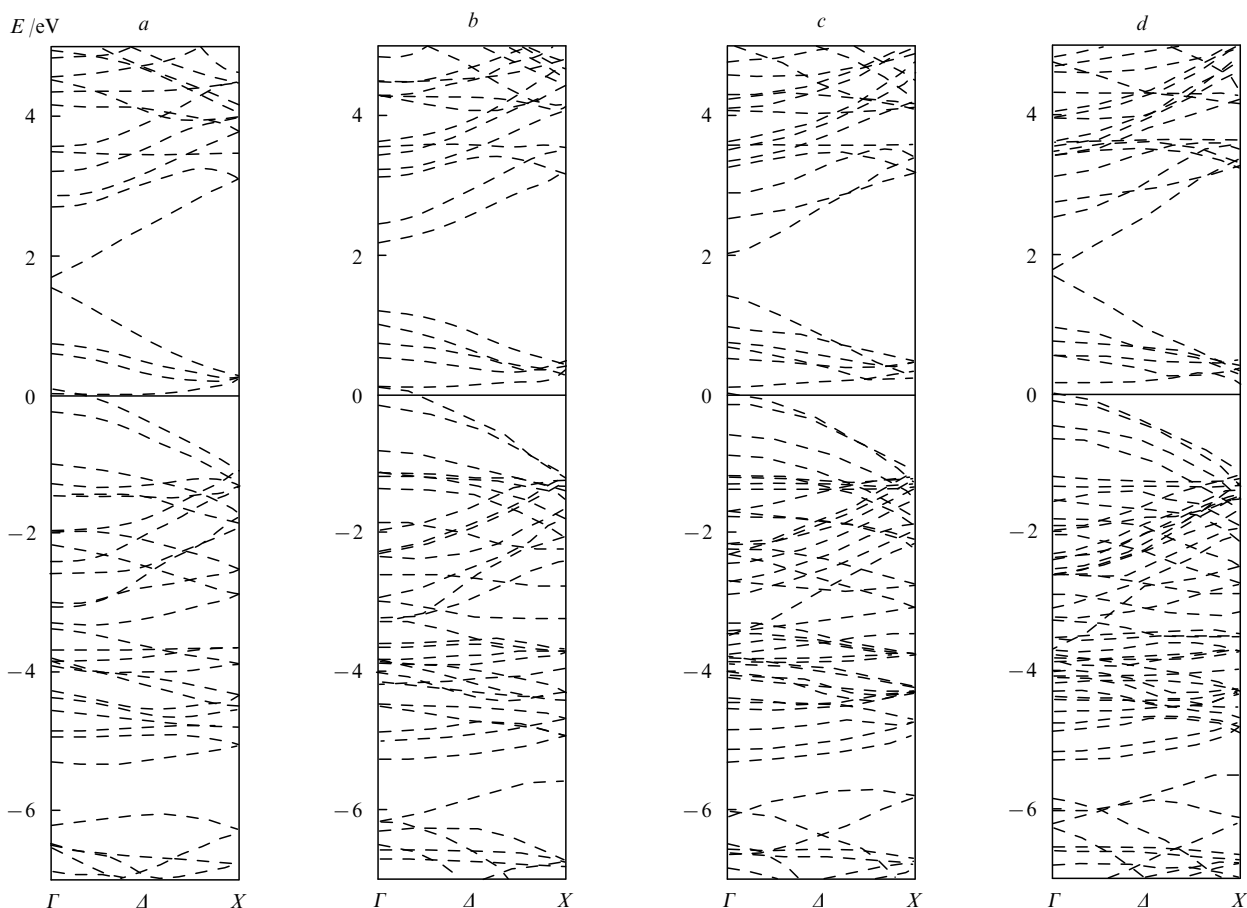


Figure 30. Band structure in achiral BC_3 nanotubes depending on their diameter. (n,m) : (a), (3,0); (b), (4,0); (c), (5,0); (d), (6,0).

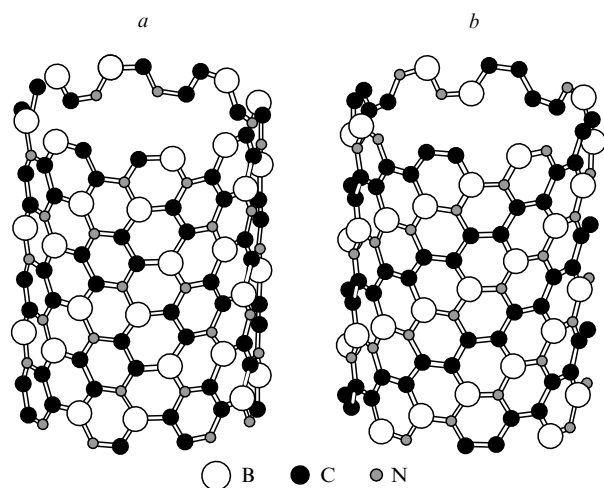


Figure 31. Possible atomic geometries of the nanotubes based on hexagonal boron carbonitride. Conductivity type: (a) *I*; (b) *II*.

Structures of graphite NT^{372, 399–406} revealed the dependence of their electronic properties on the diameter and chirality. For instance, depending on d , the conductivity type changes from semiconducting to metallic.

Attempts to forecast the electronic properties of a number of nanosized tubular structures have been made.^{407–409} These might be formed on the basis of the known layered boron-containing phases with a hexagonal lattice: h-BN, BC₂N, and BC₃.

The electronic structure of boronitride nanotubes⁴⁰⁷ was considered in terms of the Slater–Coster TB method.⁴¹⁰ It was assumed that taking into account the specific type of chemical bonding in h-BN (noticeable contribution of the ionic component), the electronic properties of NTs based on h-BN should be less sensitive to the size and structure compared to the graphite-based NT. This is of great technological importance for the preparation of nanomaterials with desired properties. As it was demonstrated,⁴⁰⁷ all NT considered are semiconductors with FG varying in the range from 4.5 to 1.0 eV with the decrease in the tube diameter. This change is related to the change in ΔE_g of h-BN under external pressure (see chapter IV). In contrast to $(n,0)$ -NT, chiral (n,m) -NT are less sensitive to variations of the diameter. Besides, $(n,0)$ -NT are semiconductors with direct FG (transition $\Gamma-\Gamma$), while (n,m) -NT have indirect FG (transition $\Delta-\Gamma$). The change in chiral angle θ (see Fig. 27) is more critical for tubes with a smaller diameter, while NT with a $d > 12$ Å possess broad FG with weak dependence on chirality. This may be qualitatively explained by the fact that the distance between the diametrically opposite boron and nitrogen atoms on the surface of NT with small radius is comparable with the interlayer separation in h-BN, so its change [depending on chirality: $d(4.0) = 6.4$ Å and $d(4.4) = 10.6$ Å] should strongly influence direct interactions between these atoms.

The above discussed energy band transformation for nanotubes of h-BN depending on their structure is illustrated in Fig. 28, where the results of a Hückel calculation for NT a h-BN⁴¹¹ are compared with the band states of isostructural carbon quasi-one-dimensional systems.

The electronic structure of NT based on the highest boron carbide BC₃, has been studied.⁴⁰⁹ In order to estimate the mechanical properties of BC₃ nanotubes, calculations of elastic deformation energies were performed that gave smaller values in comparison with graphite-like NT (Fig. 29). This may indicate higher stability of BC₃ nanotubes.⁴⁰⁹

Band structures of BC₃ $(n,0)$ -NT ($n = 3, 4, 5$, and 6) are shown in Fig. 30. The conductivity type unequivocally changes from metallic to semiconducting as the diameter increases. This effect is associated with noticeable deviations of bond angles (for NT of

small size) from 120°. As a consequence, both sp^2 - and sp^3 -hybridised atoms are involved in s-interactions. The sp^3 type determines energies of borders for valence and conductivity zones, i.e. the magnitude of FG. With the increase in the NT diameter, the interbond angles approach the limiting value in the planar net (120°), and ΔE_g for NT approaches the FG value in BC₃ single layers. More adequate studies of BC₃ nanotubes should take into consideration not only single NT, but a system of coaxial NT as well⁴⁰⁹ that can be formed by the rolling of several boron carbide nets. This is due to the fact that an account of interlayer interactions plays a decisive role in simulations of the conductivity properties of boron carbide.²²⁴

It is well established that planar nets of boron carbonitride BC₂N can manifest either the metallic or semiconducting properties depending on the ordering type of atoms therein.³⁴¹ Thus, one may expect that rolling a BC₂N single layer of the types *I* and *II* (see Fig. 24 *a,b*) into cylinders will result in NT with distinctly different properties. Geometry of BC₂N (n,n) -NT of types *I* and *II* for $n = 4$ is shown in Fig. 31. Band structure calculations by TB method⁴⁰⁸ indicate that NT with a small diameter ($n = 2$) maintain the conductivity properties typical of parent single layers. However, for (n,m) -NT of type *I* the change in the conductivity type from metallic to semiconducting, depending on diameter and chirality, is possible (like for graphite NT). Presumably, (n,n) -NT of the type *II* should be the most stable (see Fig. 31), since their atomic configuration provides the maximum number of strong C–C and B–N bonds.⁴⁰⁸

Anisotropy of conductivity in BC₂N single layers allowed one to suggest that chiral NTs can conduct helicoidal current, and therefore act as nanocoils.⁴⁰⁸ Many questions that require deep theoretical considerations are related to the capillary effect in boron-containing nanotubes. Microlevel modelling of the influence of various impurities and structural defects that can appear during synthesis on their properties is also of great significance.

One of the examples of deviations from the ‘ideal’ structure for BC₂N has been discussed.⁴⁰⁸ In the experiment, carbon atoms as an admixture substituted boron or nitrogen atoms. It was pointed out that the C→N substitution gives rise to the appearance of an acceptor level above the top of VZ by 0.03 eV, and the C→B substitution generates a donor level lower than the bottom of the conductivity zone. As a consequence, a conductivity type for semiconducting carbonitride nanotubes (n - or p -type) may be regulated by changing their stoichiometry, since the electron or hole concentration can increase in B_{1-x}C_{2+x}N or BC_{2+x}N_{1-x}, respectively.

A number of papers devoted to the synthesis of tubular carbon nanostructures containing admixtures (boron, nitrogen)^{412, 413} have been published recently.^{414–417} In particular, the topology of terminal groups in NT has been discussed.⁴¹⁷

VII. Boron phosphides and arsenides

Among the known boron phosphides and arsenides,^{5, 7, 10, 22, 32} the sphalerite-like BP and BAs attributed to semiconductor type *III–V*, are the best studied.^{258, 293, 295, 297, 302, 306, 418–423} Band structures of BP and BAs calculated by the APW method (Fig. 32) are typical of this type of semiconductors. The valence zone includes a low energy subband mainly of s -states that is separated from the zone of hybrid $p-p$ states by an energy gap, and the dispersion $E(k)$ is much larger for BAs than for BP. Most attention in the papers mentioned was paid to the estimations of the FG. Data shown in Table 9 allows one to judge the order of these values. It is clearly seen that on going from BP to BAs, ΔE_g for indirect FG decreases by ~ 1.1 eV and for direct FG increases by ~ 0.2 eV.

Calculations of the optical properties^{258, 295, 297, 302, 306, 418–423} allow reliable interpretation of the experimental results. The most intense peak $\varepsilon_2(\omega)$ for BP ($E = 6.8$ eV) is caused by the interband transition $X_{5v} \rightarrow X_{3c}$, and the next (as regards intensity), ($E = 7.6$ eV) is caused by the $\Gamma_{15v} \rightarrow \Gamma_{15c}$ transition.⁴²³ The

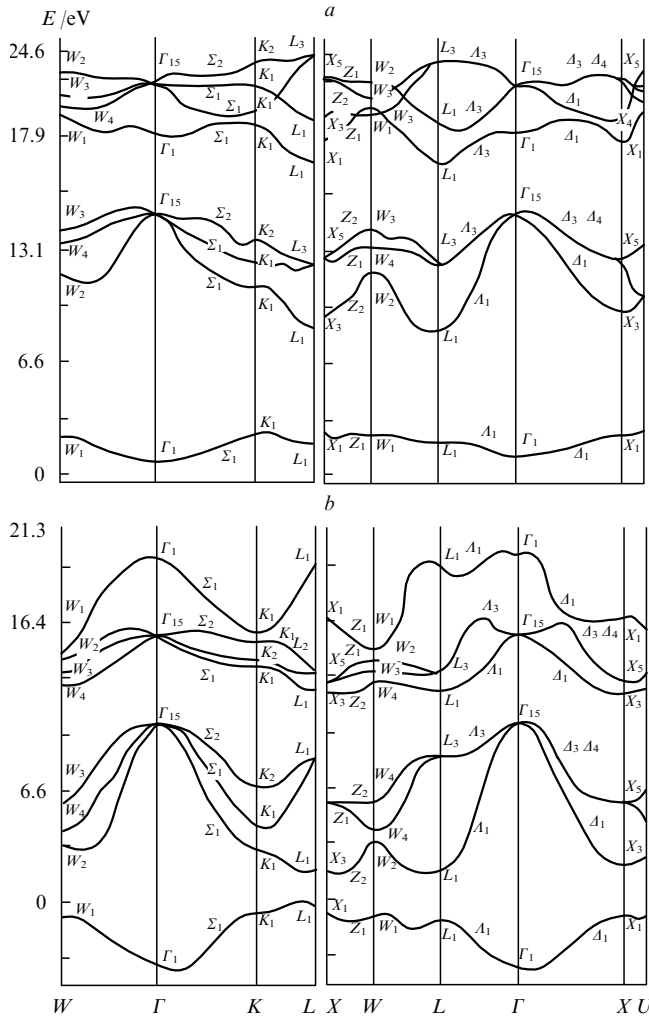


Figure 32. Valence bands of sphalerite-like BP (a) and BAs (b). APW calculations.⁴²³

Table 9. Calculated results and experimental values of direct (ΔE_g^d) and indirect (ΔE_g^i) forbidden gap, lattice constant (a), and volume modulus (B) for BP and BAs.

Parameter	Calculation	Experiment	Ref.
Results for BP			
ΔE_g^d /eV	5.0	—	297
	4.0	—	423
ΔE_g^i /eV	6.2	2.0	424, 426
	6.0	2.1	425, 427
	4.2	2.0	418, 230
	2.2	2.4	297, 428
	2.4	—	423
a /Å	4.60	4.54	315, 431
B_0 /GPa	171	173	315, 431
Results for BAs			
ΔE_g^d /eV	3.6	—	421
	4.2	—	423
ΔE_g^i /eV	1.6	1.5	421, 429
	1.3	1.4	423, 430
a /Å	4.83	4.78	315, 431
B_0 /GPa	149	—	315

maximum at the energy 5.7 eV is attributed to the $L_{3v} \rightarrow L_{1c}$ transition. For BAs, the main peak $\varepsilon_2(\omega)$ can be attributed⁴²³ to the $L_{3v} \rightarrow L_{1c}$ transition and the next one (the same as for BP) is associated with the $\Gamma_{15v} \rightarrow \Gamma_{15c}$ transition.

Band calculations of the bulk modulus and lattice constants for BP and BAs have been performed,⁴²³ the divergence with experiment did not exceed $\sim 1.5\%$ (see Table 9).

To our knowledge, only one XES study of a more complex system $\text{BP}_x\text{As}_{1-x}$ has been carried out.⁴³² Comparison of parameters of P $L_{2,3}$, P K_β , and B K_α spectra for the SS with the corresponding XES data for BP and BAs (see Refs 81, 433–436) leads to the conclusion that,⁴³² along with XES peaks that reflect P $3s, 3p - B 2p$, P $3s, 3p - B 2s$, and P $3p - B 2p$ interactions, P $L_{2,3}$, P K_β , and B K_α bands of a quasi-binary system BP-BAs constitute an additional substructure that can be attributed⁴³² to the formation of direct P–As interactions.

Data on the electronic structure of other phases that are formed in a B–(P,As) system involve only XES results for B_{12}P_2 (see Refs 81, 436) and calculations for B_{12}P_2 and B_{12}As_2 performed by the APW,⁵³ TB,¹¹⁰ and pseudopotential⁴³⁷ methods. According to,¹¹⁰ the electronic structure of B_{12}P_2 and B_{12}As_2 is close to that of $\alpha\text{-B}_{12}$. These phases have a flat valence zone with indirect FG equal to ~ 2.5 (B_{12}P_2) and ~ 2.3 eV (B_{12}As_2).

VIII. Boron oxides

In a rather numerous group of boron oxides and other more complex oxygen-containing compounds described in the literature,^{5, 7, 14, 32, 34} the EES of boron trioxide B_2O_3 ^{131, 238, 241, 438–443} and boric acid H_3BO_3 ^{131, 241, 438, 444} were extensively studied with XES, AES, and XPS. These two substances that play an important role, for instance, in the technology of boron-containing glasses, have similar crystallographic characteristics.

Preliminary studies of B K_α emission and absorption spectra for B_2O_3 ^{131, 238, 438–441} revealed a number of spectral maxima that reflect^{399–402} mixing of boron states with O $2s$ states (high wavelength satellites in XES) and O $2p$ subbands. Selective maxima in the absorption spectra can be explained by an exciton mechanism of their formation. This interpretation was qualitatively confirmed by semiempirical CNDO cluster calculations for a minimal group that model B_2O_3 (BO_3^{3-} and BO_3B clusters) and H_3BO_3 (cluster H_3BO_3).⁴⁴⁵ In particular, a low-energy absorption peak is due to an excitation of B $1s$ -electrons and their transition to vacant $2a_2$ MOs (in the MO system of BO_3^{3-}) composed of $2p_z$ -orbitals of the boron.⁴⁴⁵ The broad absorption subbands that follow in energy may be assigned to subbands of B $2p_{x,y}$ -states.

A detailed study of B_2O_3 and H_3BO_3 was carried out²⁴¹ using XES, AES, and XPS spectroscopy. Comparison of measured binding energies for B $1s$ levels in the diboron trioxide with MO calculation data⁴⁴⁵ allowed one to evaluate the effective charge on the B atoms ($+0.6$ e). Figure 33 illustrates the structure of the B_2O_3 valence band. XPS and (O,B) K_α X-ray emission spectra contain two distinct filled subbands. O $2s$ and B $2s$ states contribute to the lower subband, and the higher corresponds to a mixed B $2s - O 2p - B 2p$ type. The Fermi level coincides with a short-wavelength maximum in the B K_α spectrum.

It should be mentioned that the X-ray photoelectron spectrum reflects virtually no contribution of B $2p$ states to the VZ due to low magnitude of the photoionisation cross-section of B $2p$ states (0.0002) as compared to the others: 0.0193 (O $2p$), 0.022 (B $2s$), and 0.1405 (O $2s$).⁴⁴⁶ Two peaks in the XPS spectrum with the energies of 10.7 and 6.9 eV correspond to the peaks (11.5 and 7.2 eV) in O K_α -XES spectrum and form the II doublet band (see Fig. 33) that overlaps the broad subband with a maximum at 14.4 eV (peak I). Taking into account the values of photoionisation cross-sections, the latter can be attributed to B $2s$ states. Comparison of experimental intensities for peaks I and II with theoretical values obtained under assumption of atomic and hybrid sp^2 -configuration of the atomic components allows one to suggest the presence of covalent bonds in the planar layers

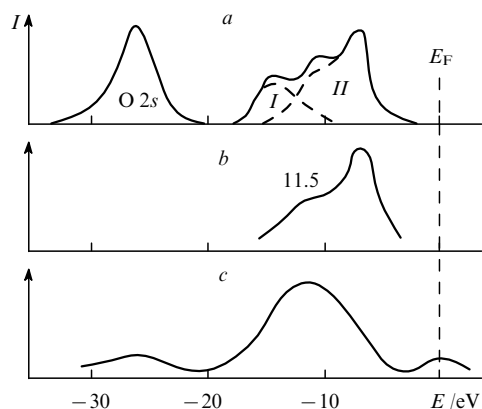


Figure 33. XPS (a) and X-ray emission O K_{α} (b) and B K_{α} (c) spectra of B_2O_3 .

composed of atomic triangles (the crystal structure of B_2O_3 is described, for example, in Refs 447–449) and formed mainly due to the B ($2p$)–O ($2p$)–B ($2s$) overlap.

Results of B_2O_3 and H_3BO_3 studies by secondary ion mass spectrometry²⁴¹ indicate a weakening of several B–O bonds in boric acid in comparison with diboron trioxide. It may be attributed to the formation of additional O–H interactions in H_3BO_3 .

Auger electron spectra for B_2O_3 and H_3BO_3 (Fig. 34) consist of six distinct peaks.^{241, 450} Calculations of the possible KLL Auger transitions, including interatomic ones, were performed²⁴¹ using binding energy values for core and valence states. It was demonstrated that peaks 5 and 6 are due to several probable transitions of the KLL series, and the low energy peaks 1–4 probably have a plasmon nature. More narrow peaks for H_3BO_3 might indicate the simpler structure of the VZ for boric acid in comparison with that of B_2O_3 .²⁴¹

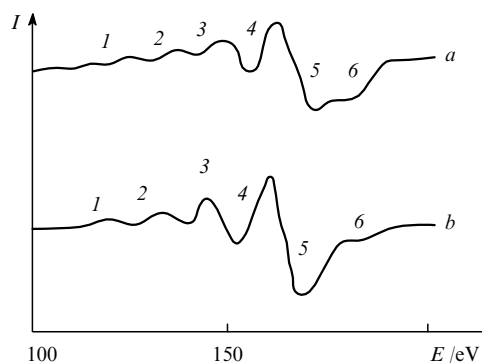


Figure 34. Derivative AES spectra of B_2O_3 (a) and H_3BO_3 (b). 1 to 6 see text.

Further studies of B K_{α} -XES for B_2O_3 ^{443, 444} have confirmed a typical three-peak structure of the spectrum; its interpretation has been proposed. A low-energy maximum (K_{α} satellite separated by ~ 14.5 eV from the main peak) is formed due to a contribution of p-states of the emitting centre to the O ($2s$) subband. High-energy substructure of K_{α} spectrum near the absorption edge have a resonance nature.⁴⁴⁴ It is formed with participation of orbitals attributed to virtual levels with π^* symmetry (in the non-excited state). In order to confirm it, B K_{α} bands for a number of minerals { $AlBO_3$, $Be_2(BO_3)OH$, $Mg[(OH)_3BOB(OH)_3]$, $CaB_2Si_2O_8$, BPO_3 }, where the first two species contain boron in trigonal coordination and the other — in tetragonal coordination, were compared.⁴⁴⁴ B K_{α} XES spectra contain a prominent high-energy satellite (for trigonal coordination the lowest unoccupied states

have σ^* and π^* symmetry), although for the tetragonal coordination (with unoccupied states of only σ^* symmetry) this spectral maximum is virtually absent.

B K_{α} spectrum of boron suboxide $B_{13}O_2$ was also studied.⁷⁷ Oxygen atoms in this structure form O–B–O chains between B_{12} icosahedra.⁴⁵¹ Therefore, the emission line of the sesquioxide appears to be very similar to that in α - B_{12} . However, the width of the B K_{α} band for $B_{13}O_2$ is ~ 0.3 eV less than in the crystalline α -boron.

The detailed description of the chemical bonding nature and EES features for the boron oxides definitely requires quantum chemistry calculations.

IX. Conclusion

This paper reviews data on several classes of solid state compounds of boron with nonmetals most frequently studied by quantum chemistry methods. Fundamental and technological properties of other borides of nonmetals either in the crystalline or molecular state, *i.e.* boron hydrides (boranes), halogenides, silicides, *etc.* are also of great interest.

Studies of properties of the borides considered above, and their application in the search for new high-technology materials are developing intensively. This can be judged, in particular, by the range of problems discussed at the International Symposium on boron and borides: investigations in the field of the amorphous state of boron; boron doped with different dopants (including transition and rare-earth metals); amorphous alloys of boron; the role of nonmetallic borides in thin-film technology; problems of deposition and functionality of boron-containing coatings; polytypism among borides; factors which determine polytypes formation; ultradispersed and single crystal borides and their properties; design of supersolid materials, multi-purpose ceramics (B_4C – TiB_2 , Al – B – C , Al – B – Ti , *etc.*), bi- and multi-layer composite materials with borides.

These trends in the investigation of material science of borides, in our opinion, will determine the principal directions in the development of theoretical quantum chemistry models, methods for the description and prediction of properties of borides.

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Energy exchange and reactions of highly excited polyatomic molecules

I S Zaslanko

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Abstract. The advances in the study of energy exchange in the reactions of highly excited polyatomic molecules are analysed. The possibilities of spectroscopic methods for the observation of nonequilibrium energy distributions are demonstrated. Various models of intramolecular and intermolecular energy exchange as well as the reactions of highly excited states of polyatomic molecules are considered: spontaneous unimolecular decomposition and bimolecular reactions. Application of emission techniques in the visible, UV and IR spectral regions, both in the traditional version and especially with Fourier transformation, is very effective for detection of distributions of highly excited states in reacting systems with thermal and laser pumping. Several predictive comments are made in conclusion. The bibliography includes 130 references.

I. Introduction

The history of chemical kinetics is indissolubly linked with the reactivity of highly excited molecules.^{1–3} The rates of the vast majority of reactions depend significantly on the fraction of species where the internal degrees of freedom contain an amount of energy comparable to the reaction threshold E_0 or the barrier E_d separating the electronic configuration of the products from that of the reactants.

In the case of highly excited molecules, the number of species capable of reacting is determined by the simultaneous influence of many elementary processes — nonelastic scattering (energy exchange), collisions with rearrangement (chemical reactions), and interactions with external fields.

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The macroscopic experimentally measured rate constant has an internal structure reflecting the relationship (frequently sophisticated) between the energy exchange processes and chemical reactions. The first and hitherto unsurpassed advance in the elucidation of this internal structure is the statistical theory of unimolecular reactions.^{4–8} By virtue of the distinct physical basis and the high degree of development of the computational methods, this theory has found so many applications that it has stimulated the extension of the 'unimolecular ideology' to the entire wide variety of bimolecular reactions. The achievements in this field are illustrated in the present review.

In the case of rapid energy exchange, the distribution of the reactants with respect to rates and energy levels corresponds to equilibrium. Under these conditions, the kinetics of chemical reactions are described by equations for concentrations which include the rate constants averaged thermally and the reaction rates are determined solely by the pressure, temperature, and mixture composition.

The development of experimental techniques and the requirements of modern technology have favoured a shift of the interest of investigators into the field of study of rapid reactions, which not only compete with energy exchange processes and processes involving the establishment of distributions but under certain specific conditions fully determine the form of these distributions.

For molecules with a small number of atoms and low excitation energies, the necessary information about the elementary processes is usually obtained in beam experiments, with laser methods for the generation of beam species in well defined quantum states and laser methods for the observation of the states of the product species.

By virtue of the progress in the development of computational techniques in quantum chemistry and in atomic collision theory, it has become possible to obtain reliable information about the elementary processes also by purely computational methods.^{5,6} For polyatomic and highly excited molecules, these methods are being used with increasing frequency and the reviews in this field therefore rapidly become obsolete.

Molecular spectroscopy has exerted a definite influence on the establishment of the fundamental concept associated with molecular structure. The 'kinetic' aspect appeared in this field in

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connection with the study of the absorption spectra of unstable species. The direct kinetic application of spectroscopy involves the analysis of the width of spectral lines. The CH_3 radical may serve as a characteristic example. Its predissociative line width of 60 cm^{-1} in the 216 nm absorption band^{9,10} may be assigned to a predissociative lifetime of $\sim 88\text{ fs}$ (for CD_3 , the corresponding values are 8 cm^{-1} and 663 fs , which can be accounted for by the considerable isotope effect). After four decades of experimental studies in this field, the number of examples of this kind has increased greatly and the range of lifetimes extends from femtoseconds to microseconds.

Later examples, associated with molecular dynamics, include nonradiative transitions in polyatomic molecules (see, for example, Jortner and Bixon¹¹) and also the interaction of coherent laser radiation with molecular systems.^{7, 12, 13}

Analysis of the possibilities of spectroscopic methods together with the description of their applications to specific systems represents the main content of the present review.

II. Molecular kinetics and molecular spectroscopy

The extensive introduction of spectroscopic methods into chemical kinetics during the last 30 years has completely altered its features and has caused a shift in priorities. The subdivision of the methods of study employed into 'direct' and 'indirect' has little justification. Firstly, there are no methods which would yield kinetic information without interpretation within the framework of some kind of model. Secondly, the systemic approach with analysis of the entire available information is the most productive.

The true history of any science is the history of concepts. In this respect too, the kinetics of unimolecular reactions yield a striking example of the way that the use of indirect methods has created a firm basis, which was merely strengthened on subsequent application of the entire available range of modern optical spectroscopic techniques.

In fact, all the principal concepts constituting the foundation of the modern theory of unimolecular reactions have been formulated on the basis of experiments carried out by traditional methods of chemical kinetics:⁴ the identification of the stages involving activation and spontaneous decomposition of the active molecules; the concept of a quasi-continuum of vibrational-rotational states; the correct estimation of the intramolecular relaxation time of the vibrational energy of active molecules.

Paradoxically, after the discovery of the IR laser-induced dissociation of polyatomic molecules, many efforts were wasted on attempts to interpret the results within the framework of modified one-oscillator models before it was recognised that the principal results fit within the framework of the Rice–Ramsperger–Kassel–Marcus (RRKM) theory, which had already been used by kineticists for many years.

1. Models of polyatomic molecules for kinetic applications

Qualitatively new features, consisting of an increase in the density of states and a considerable acceleration of the energy exchange between them, arise in polyatomic and highly excited molecules. As a consequence of the rapid intramolecular energy exchange (electronic-vibrational conversion, intermode transitions, or rotational-vibrational exchange), with increase in the excitation energy the simple picture of motion, characteristic of molecules with a small number of atoms or weakly excited molecules, disintegrates. The energy spectrum becomes much more complex because vibrational motion becomes stochastic.⁷

A high degree of specification of details in the description of the structure of a polyatomic molecule is not required for kinetic applications or for the interpretation of the results of measurements with a moderate spectroscopic resolution. Fig. 1 presents the simplest scheme, which clearly illustrates the majority of the phenomena discussed in the present review. A 'spaced out' vibrational spectrum in the lower parts of the ground and electronically excited terms, transforms into a quasi-continuum with rapid

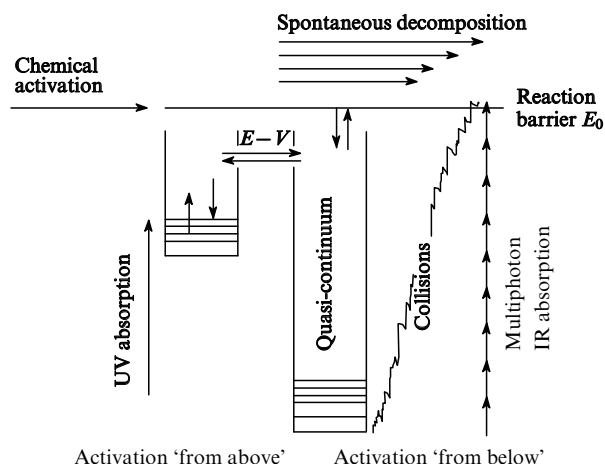


Figure 1. Principal kinetic processes in the activation of a polyatomic molecule.

mixing of the vibrational modes. The types of activation ('from below' and 'from above') are indicated. The vertical arrows designate the collision and vibrational-translational ($V-T$) transitions, whilst the horizontal arrows designate chemical reactions: on the left — activation as a result of exothermic chemical reactions, on the right — spontaneous decomposition, which intensifies with increase in the vibrational energy; $E-V$ represents the electronic-vibrational exchange between the terms.

Any external influence on the molecular system leads rise to a nonequilibrium distribution with respect to energy levels, the form of which is determined by the competition between the pumping and relaxation processes and chemical reactions.

The methods for the interpretation of non equilibrium energy distributions have also developed in parallel with the development of diagnostic methods in relation to highly excited states (HES). In this connection, it is instructive to turn to the hierarchical picture of the models of nonequilibrium processes (specifically, we have in mind the unimolecular decomposition reactions):

the two-level Lindemann scheme for unimolecular decomposition deals with the ground state of a polyatomic molecule and its excited (active) state in the region of the barrier to chemical reactions; this model operates with the corresponding kinetic equations for the concentrations of above states and yields a level of description necessary for the interpretation of macroscopic rate constants;

the model based on the use of the concept of the vibrational temperature T_v for a separate ensemble of vibrational degrees of freedom, which, generally speaking, is not in equilibrium with the surrounding gas at a temperature T_g ; in fact, in this description the form of the nonequilibrium distribution function is assumed to be identical with the Boltzmann distribution; in order to find T_v , the system of chemical kinetic equations is supplemented by the balance equation for the vibrational energy and then the rate constant for unimolecular decomposition is a function of two temperatures — T_v and T_g ; ^{10–17}

interpretation of kinetics 'in the language' of the distribution function with respect to the internal energy of molecules; the experimental data are analysed using the solution of the fundamental microkinetic equation [(FME) — master equation].

With the aid of Fig. 1, it is convenient to elucidate the sense of the term 'highly excited states' of polyatomic molecules. In the context of the current review, these are states for which there is no possibility of subdividing vibrations into modes and the energy of which is consequently higher than the threshold of the transition of vibrational motion to the stochastic regime.

2. Spectroscopic methods for the study of highly excited molecules

Highly excited states of molecules with average energies $\langle E \rangle \simeq E_0$ may be obtained as a result of the thermal heating by a shock wave, single photon optical excitation with subsequent intramolecular $E-V$ conversion, or multiphoton excitation in the field of intense IR radiation, electron impact, *etc.*^{14–16}

Mainly optical methods are used for the recording of HES and for the observation of energy distributions, although others, for example corpuscular or field methods, may also be useful. There are many versions of optical methods, for example the absorption and emission methods, in which the radiation in various wavelength ranges (IR, visible, UV) is used. The optical methods are characterised by a high time resolution and yield the most complete information about the evolution of intramolecular and intermolecular energy distributions.

The methods for the study of the collision deactivation of the HES of polyatomic molecules may be divided into two groups. The methods of the first group are used to record processes associated with the highly excited molecules themselves, whilst those of the second group record the responses of the surrounding system to the HES relaxation process. The thermal lens¹⁷ and optoacoustic methods have been used to find the energy flux from the HES to the translational degrees of freedom in the course of relaxation.^{9,18} The methods involving the recording of the HES themselves belong to the group of methods with the highest information content.

3. Characteristic features of the principal methods for the generation of HES

The advantages and disadvantages of various methods for the generation of HES are determined by the degree of their universality, the range of available energies, and the possibility of the establishment of HES distributions of a specified type. The types of activation considered below are illustrated in Fig. 1.

The thermal heating method, which can be readily applied in experiments with shock waves, is one of the most universal. It makes it possible to achieve a virtually instantaneous heating of molecules to temperatures of several thousands of degrees.

The method involving the resonance multiphoton IR excitation of polyatomic molecules has come to be widely employed immediately after the appearance of CO₂ pulse lasers.^{7,9,12,13} At the present time, the physics of the interaction of the intense IR radiation with polyatomic molecules has been examined in numerous publications in which all the principal features of this method for the study of the spectra and reactions of HES are dealt with. The resonance pumping of molecules by an IR laser in the pulse regime makes it possible to obtain HES over a period $t \simeq 10^{-8}$ s, whereupon the molecules form two ensembles — ‘cold’ and ‘hot’. (The temperature of the latter may reach thousands of degrees.)

The single-photon UV excitation method (with subsequent intramolecular $E-V$ conversion) is used to generate the HES of molecules having an electronically excited state in the range of energies investigated. This state is mixed by a nonadiabatic interaction with the high vibrational levels of the ground state. Typical examples of such molecules are SO₂ and NO₂. The energies of the initial excitation, accessible to the resonance single-photon UV excitation method, are of the order of several electron-volts. The initial energy distributions of the HES are close to the δ -distributions and may be regarded as microcanonical.

4. Molecular spectroscopy and the development of methods for the study of highly excited states

Molecular spectroscopy is one of the principal methods yielding information about the dynamics of processes involving the HES of polyatomic molecules. Bearing in mind the special interest in the purely chemical aspects of such processes, we have given preference to the absorption-emission diagnostics based on moderate

spectral resolution with a characteristic time range of 0.1–1000 μ s.

If an external perturbation induces a jump in one or several parameters (temperature, pressure, electric field strength, or another macroscopic parameter), then the subsequent evolution of the system towards an equilibrium state (or most often a quasi-stationary state) can be monitored by classical kinetic spectroscopic methods.^{2,7,9}

The time resolution of flash photolysis has increased during the last 30 years from microseconds to femtoseconds and, when combined with coherent spectroscopic methods in the femtosecond range, this makes it possible to follow the real dynamics of the formation and dissociation of chemical bonds.

In contrast to the classical kinetic spectroscopic technique, which is designed primarily for the investigation of the so called global reaction mechanism and the corresponding rate constants, the modern technique employing laser methods in molecular beams with coherent nanosecond and femtosecond pulses, leads to the possibility of the observation of the detailed features of molecular dynamics.^{19,20} Several scientific centres, particularly those with the necessary financial resources, are leaders in research of this kind.[†]

5. The method of competing channels with application of fluorescence spectroscopy

The initial concepts of the method of competing channels using fluorescence spectroscopy arose in relation to proton and electron transfer processes in solutions.²⁰ Later this method came to be widely employed for the study of intramolecular kinetics and of the redistribution of vibrational energy in electronically-excited states of polyatomic molecules.^{21,22} An essentially analogous approach has been applied in experiments with chemical activation and intramolecular relaxation²³ under the conditions of stationary photolysis at high pressures,²⁴ where collisions in a gas are used as a time reference standard (‘clock’). However, it is not always easy to answer the question which particular competing channels have to be considered in interpreting the results.

6. The line form in optical spectra

The Lorentzian optical line width Γ in optical spectra may be related to the rate constant k for a quasi-unimolecular process by the simple equation

$$k = \frac{2\pi\Gamma}{\hbar},$$

where $\hbar$ is the Planck constant.

Predissociation and similar processes are suitable examples of the applicability of this approach. The same method has been used to record high overtones for polyatomic molecules under beam conditions in order to obtain information about the rates of relaxation processes,^{25,26} but it is then necessary to take into account very thoroughly the contributions of the uniform and nonuniform line broadening.^{27,28}

Detailed analysis of the experimental methods used to investigate the dynamics of the HES of polyatomic molecules is an object of separate detailed consideration. In this communication, these methods will not be dealt with. In order to obtain an idea about the modern diagnostic possibilities, one may refer to monographs and reviews.^{9,12,13,29}

Amongst spectroscopic methods, the laser methods involving molecular beams with application of the Fourier transformation

[†] The experimental technique has become so complex in this case too that the maintenance of a prestige level of research has become more of a contest between capacities for investment rather than between concepts. Furthermore, one should note also a degree of uncertainty in the interpretation of the results of measurements with ultrashort pulses — the rate of some kind of fast process is measured but it is sometimes not understood which particular process this is.⁹

of the spectra are correctly regarded as the most fruitful for the study of processes with participation of HES.

The possibilities of various optical methods for the probing of molecules and radicals using laser radiation sources have been described in fair detail in reviews.^{9,29} The high spectroscopic resolution of these methods makes it possible to employ them for the detection of species in fixed quantum states, but in the study of the kinetics of energy exchange, unimolecular decomposition, and bimolecular reactions the simpler and at the same time fairly informative absorption methods with a moderate spectral resolution are preferable. These methods have in fact proved to be the most convenient to obtain the isoenergetic distributions $f(\langle E \rangle)$ which enter into the fundamental microkinetic equation (FME).

III. Molecular 'hot' band absorption spectroscopy

1. Fundamental relations

It is known that the UV absorption spectra of many polyatomic molecules have the characteristic form of bell-shaped curves with temperature-dependent moments.^{10,30} With increase in temperature, the spectra shift towards the long-wavelength region and are broadened; a molecular 'hot' band is then said to be produced. It is related to the increase in the population of the excited molecules (Fig. 2).

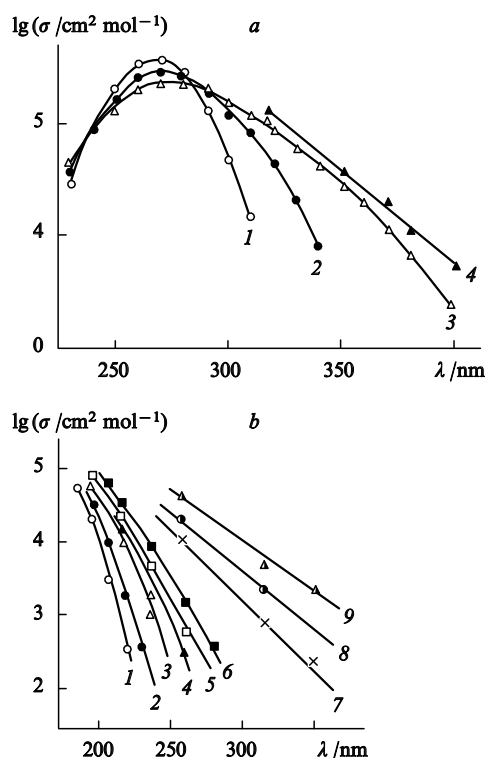


Figure 2. Dependence of the absorption cross-section for the 'hot' bands of the CF_3I (a) and N_2O (b) molecules on the wavelength. $T(\text{K})$: a: (1) 300; (2) 625; (3) 1050; (4) 1250; b: (1) 300; (2) 470; (3) 670; (4) 770; (5) 870; (6) 950; (7) 1430; (8) 1620; (9) 2070.

The 'quasi-diatomic' molecule model, with the linear-oscillator fitting of the terms between which a vertical transition takes place following the absorption of a photon, is used for the simplest interpretation of these spectra. Subject to additional hypotheses concerning the nature of the fitting³¹ of the wave functions for the dissociated states of the electronically excited molecule and the independence of the transition point of the vibrational energy of the initial state, the linear-oscillator model of the vertical transitions leads to the well known Wieland–Sulzer formula³²

$$\sigma(\nu, T) = \sigma_0 \text{th} \left(\frac{\theta}{2T} \right)^{1/2} \exp \left[\text{th} \left(\frac{\theta}{2T} \right) \left(\frac{\nu - \nu_0}{\Delta \nu} \right)^2 \right]. \quad (1)$$

Here $\sigma(\nu, T)$ is the experimentally measured absorption cross-section, σ_0 a phenomenological parameter, θ the vibrational quantum of the oscillator, ν the optical transition frequency, ν_0 the frequency of the vertical transition from the equilibrium position, $\Delta \nu = F^2/\mu\theta$, F the strength of the interatomic interaction in the dissociated state, and μ the reduced mass.

Formula (1) describes fairly well the form of the main part of the absorption spectrum, but it does not take into account the weak but experimentally clearly observed shift of the maximum of the absorption curve.^{32,33} The temperature dependence of the absorption cross-section can be obtained if account is taken in the calculation of $\sigma(\nu, T)$ of the anharmonicity of the vibrations, the curvature of the form of the electronically excited state, or the dependence of the electronic matrix element on the interatomic coordinate.^{34,35} Here it is also possible to eliminate the systematically observed discrepancy between theory and the measured quantities in the long-wavelength region.

For the Morse exponential model, the parameters of the interaction potential are expressed by the relations

$$U_i(R) = D[1 - \exp(-\alpha R)]^2,$$

$$U_f(R) = A \exp(-\beta R) + \Delta,$$

$$M_{if}(R) = M_{if}(0) \exp(\alpha R).$$

where D , α , A , β , and Δ are the parameters of the potential in the initial (i) and final (f) states as a function of the interatomic distance R (the numerical values for the CF_3I molecule have been published³⁴), U_i and U_f are the electronic terms of the molecule before and after the absorption of a photon, and M_{if} is the electronic matrix element.

The Gaussian fit to the central part of the absorption spectrum (*i.e.* the generalised Wieland–Sulzer formula) was first obtained by Dalidchik *et al.*³⁴ It was established that the first moments of the absorption spectrum are a little 'sensitive' to the form of the distribution of the molecules with respect to vibrational levels, but do depend on the dynamic parameters of the model and on the average energy of the initial excitation $\langle E \rangle$. Optical measurements in the central part of the absorption spectrum may be used either for the determination of the parameters of the potential curves or for the measurement of the first moment of the vibrational energy distribution function.

Numerous examples of the measurements of $\langle E \rangle$ based on the UV absorption spectra have been published by Troe and co-workers,^{14,36–39} Letokhov and coworkers,^{12,40–42} and other investigators.^{43,44} However, the possibilities of UV absorption spectroscopy are not restricted solely to the measurement of the average excitation energy. It has been shown⁴⁵ that the long-wavelength edges of the absorption spectra of CF_3I and N_2O exhibit a distinct Arrhenius relation:

$$\sigma(\nu, T) \simeq \exp \left(-\frac{E_a(\nu)}{T} \right),$$

where $E_a(\nu)$ is the activation energy, which decreases monotonically with increase in the photon frequency ν .

Within the framework of the one-dimensional model, *i.e.* in terms of the 'quasi-diatomic molecule' approximation, such relations can be understood if use is made of the concept of vertical transitions between classical turning points.

The classical approximation may be used if the contributions of the ground and weakly excited vibrational states are negligible at the given absorption frequency. The corresponding criteria, quoted by Dalidchik *et al.*,³⁴ usually hold in the long-wavelength region.

In the classical approximation for the one-dimensional model, the average photoabsorption cross-section assumes the form^{34,35,46}

$$\sigma(v) = \frac{4}{3} \pi v f\{U_i[R_0(v)]\} |\{M_{ij}[R_0(v)]\}^2 [U_i'(R_0) - U_f'(R_0)]|. \quad (2)$$

Here $f(U_i)$ is the normalised distribution of molecules with respect to vibrational energy and $R_0(v)$ is the root of the equation

$$U_i(R) + v = U_f(R), \quad (3)$$

where U_f is the potential energy surface for the electronically excited state of the molecule.

The results of absorption measurements in the long-wavelength region are related directly to the vibrational energy distribution of molecules [see Eqn (2)].

Eqns (2) and (3), which demonstrate the possibilities of the UV absorption technique, can be applied directly only in the case of diatomic molecules. On the other hand, experiment has shown that, for a reasonable parametrisation Eqns (2) and (3) can be used successfully also for the interpretation of the UV absorption spectra of more complex molecules such as those of CS_2 ,³⁶ N_2O ,⁴⁵ SO_2 ,⁴⁷ etc.

When the spectra of complex molecules are described in terms of the formulae of the one-dimensional model, the theory of the UV absorption method is faced by the fundamental question of the physical significance of the concept of the 'optically active' oscillator in the most general form.⁴⁶

The multidimensional generalisation of formula (2) assumes the form

$$\sigma(v) = \sigma^0 f\{U_i[R_0(v)]\}, \quad (4)$$

where σ^0 is a known multiplier which varies little, quoted by Dalidchik *et al.*,⁴⁶ U_i the potential energy surface of the molecule in the initial electronic state, and $R_0(v)$ the trajectory of the coordinate of the absolute minimum of the function $U_i(R)$ on the hypersurface $\sum(v)$, satisfying the condition for the classical vertical transition (3) (R is the set of all vibrational coordinates).

For equilibrium conditions,

$$f(U_i) = N \exp\left(-\frac{U_i}{T}\right),$$

i.e. the role of the 'activation energy' for the absorption spectrum is assumed by the function $U_i[R_0(v)]$.

Having compared Eqn (4) with the corresponding classical expression for the one-dimensional model, it is possible to elucidate the significance of the concept of the 'optically active' oscillator. In the vicinity of the extremum, $v = v_0$, where v_0 is the root of the equation

$$\frac{d}{dv} U_i[R_0(v)] = 0,$$

the function $f\{U_i[R_0(v)]\}$ may be fitted by a Gaussian function. For agreement with the results based on the one-dimensional model, it is then sufficient that the following simple condition should hold:

$$\frac{d^2}{dv^2} U_i[R_0(v)] = 0.$$

The 'optically active' oscillator is identical with the n th normal oscillator if the trajectory of the point $R_0(v)$ lies in a plane which is sufficiently close to the oscillations plane of the n th normal oscillator.^{34,35}

Experimental data (Fig. 2) as well as the results of the numerical solution of Eqn (4) for the two-dimensional model of the photodissociation of the CF_3I molecule^{46,48} have shown that, in the photodissociation of this molecule, the conditions for which the quasi-diatomic approximation may be applied holds satisfactorily (at any rate for $\lambda > 300$ nm), so that the 'optically active' oscillator may be identified with the stretching vibration of the C–I bond.

The formalism developed for the description of 'hot absorption bands' has in the main proved suitable also for the description

of the characteristics of heated molecular gases. The possibilities of the emission diagnostics for HES have been clearly demonstrated⁴⁵ and are also briefly considered below in connection with the survey of the results of the study of the wave characteristics of the relaxation of the HES.

2. 'Calibration' of absorption and emission spectra

The main result of the above analysis of 'hot' absorption bands is that the absorption cross-section for the far wing is proportional to the HES population [Eqns (2) and (4)]. However, the effectiveness of a specific application of the relations obtained depends in many respects on how well the disposition of the terms is known. The exact knowledge of these parameters is an exception rather than the rule. The role of the empirical information about the temperature and frequency dependences of the absorption cross-section for the test molecules therefore increases.

A sufficiently complete amount of information of this kind is obtained when shock-wave heating is employed. The essential feature of the approach, developed by Zaslonko and co-workers,^{45,46} reduces to the following. It is necessary to measure the relation $\sigma(v, T)$ at temperatures and pressures which guarantee the equilibrium distribution with respect to energy. The principal factor which prevents the maintenance of equilibrium is the reaction of the HES in the region of chemical reaction barriers. For unimolecular decomposition, equilibration implies that the reaction occurs at the high pressure limit, whilst for bimolecular processes this entails the occurrence of the reaction at low concentrations of the reactants whereupon the distorting influence of the reaction is minimal.

Thus when equilibrium has been attained, the equation for the absorption cross-section 'activation energy' can be represented in the following form:

$$E_i = E_v + \bar{E}_v + \bar{E}_r,$$

where E_i is the energy of the vibrational state, E_v the absorption cross-section activation energy, and $\bar{E}_v$ and $\bar{E}_r$ are the average vibrational and rotational energies of the excited molecule.

The dependences of the energy levels of the excited states, obtained in the calibration of the 'hot' absorption bands and on the basis of the thermal emission of SO_2 and NO_2 , on the transition wavelength are presented in Fig. 3. Evidently the combination of the absorption and emission methods is applicable to a wide range of energies of the excited states. Here we are dealing with differentiated optically active states. In order to apply these methods in the kinetics of nonequilibrium processes, it is necessary to find the relation between the population of optically active molecular states and total vibrational energy of the molecules.

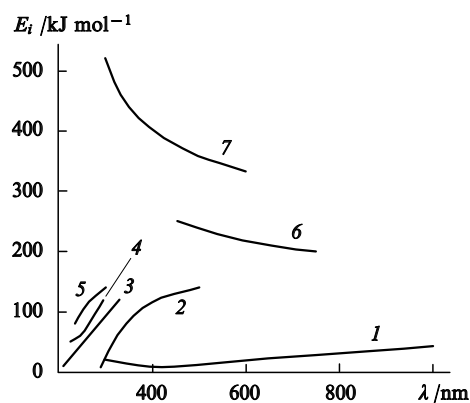


Figure 3. Dependence of the recorded excitation energy of the optically differentiated states of some molecules on the transition wavelength. Absorption: (1) NO_2 ; (2) SO_2 ; (3) N_2O ; (4) CS_2 ; (5) CO_2 ; emission: (6) NO_2 ; (7) SO_2 .

IV. Relation between the partial and total distribution functions with respect to the vibrational energy of polyatomic molecules

It is necessary to emphasise the differences in the description of processes involving HES in spectroscopy and kinetics. In kinetics, the principal parameter is the total HES energy, whilst in spectroscopy it is the population of an optically active oscillator or group of oscillators.

The vibrational energy distributions obtained on the basis of the analysis of the ‘hot’ bands in the absorption-emission spectra, refer to an optically active vibration of the molecule. In contrast to the distribution function (DF) with respect to the total energy, such distributions will be referred to as partial (PDF). The total number of independent partial distributions is equal to the number of normal vibration modes in the molecule.

In the solution of problems in chemical and molecular kinetics, we are as a rule interested in the distribution with respect to the total energy. In this connection the problem of finding the DF with respect to the total energy from spectroscopic PDF measurements arises.

The method for the finding of a relation between the PDF and the DF⁴⁹ is based on the hypothesis that, during the period of the observation of the PDF, there is sufficient time for the total energy of the molecule to be randomly redistributed between all the types of vibrations of the polyatomic molecule.[‡] The probability of observing a molecule with an energy E_i of a differentiated type of vibration for the total energy E is specified by the conventional distribution $\varphi(E_i|E)$, which is proportional to the number of states accessible for the specified E and E_i :

$$\varphi(E_i|E) = \frac{\rho_i(E_i)\rho_{s-i}(E-E_i)}{\rho_s(E)}.$$

Here $\rho_i(E)$ and $\rho_{s-i}(E-E_i)$ are respectively the densities of states of the differentiated (i) and remaining ($s-i$) oscillators of a polyatomic molecule in which the number of modes is s and $\rho_s(E)$ is the total density of states of a molecule with a total energy E .

In order to obtain the partial distribution function $f_i(E_i)$, it is necessary to average $\varphi(E_i|E)$ with respect to the total energy distribution $f(E)$:

$$f_i(E_i) = \int_{E_i}^{\infty} \varphi(E_i|E)f(E)dE. \quad (5)$$

Eqn (5) serves as a basis for the reconstruction of the DF from the experimentally measured PDF, since it establishes a mutually unambiguous relation between them.

It is convenient to express Eqn (5) in terms of the dimensionless Boltzmann distributions $f_{i0}(E_i)$ and $f_0(E)$ and the functions $h_i(E_i) = f_i(E_i)/f_{i0}(E_i)$ and $h(E) = f(E)/f_0(E)$. The Boltzmann distribution is specified in the form

$$f_0(E) = \frac{\rho(E)}{Q} \exp\left(-\frac{E}{RT}\right),$$

where $\rho(E)$ is the density of the spectrum and Q the vibrational partition function.

Taking into account this relation, we express Eqn (5) in the form

$$h_i(E_i) = \frac{Q_i(T)}{Q_s(T)} \int_{E_i}^{\infty} h(E)\rho_{s-1}(E-E_i) \exp\left(-\frac{E-E_i}{RT}\right)dE, \quad (6)$$

where Q_i and Q_s are respectively the partial and total vibrational partition functions.

It is useful to examine certain limiting cases. In particular, it follows from Eqn (6) that, if the distribution with respect to total energy corresponds to equilibrium [$h(E) = 1$], then the PDF also corresponds to equilibrium [$h_i(E_i) = 1$]. In the other limiting case for the δ -distribution, $f(E) = \delta(E-E^*)$, where E^* is the total excitation energy, the PDF is defined by the microcanonical distribution

$$f_i(E_i) = \varphi(E_i|E^*).$$

The relation between $f(E)$ and $f_i(E_i)$ is found from the integral transformation of Eqn (5). In the general case, this cannot be done analytically. If the Whitten–Rabinovitch approximation⁴ is used for the density of states, *i.e.*

$$\rho_n(E) = \frac{[E + a_n(E)E_{z_n}]^{n-1}}{(n-1)! \prod_n \hbar \nu_n}, \quad (7)$$

where $a_n(E)$ is a parameter close to unity and is weakly dependent on E ^{4, 8, 50} and

$$E_{z_n} = \frac{1}{2} \sum_{k=1}^n \hbar \nu_k,$$

is the energy of the zero-point vibrations of n vibrational modes of the molecule, then the problem may be solved.

For sufficiently high values of the total energy, it is possible to neglect the energy of the zero-point vibrations in Eqn (7). The integral Eqn (6) may be solved with the aid of the Laplace transformation.⁴ Direct substitution of the equation

$$h(E) = \frac{(s-i) \prod_k \hbar \nu_k Q_{s-i}}{Q_i} \left(\exp \frac{E}{RT} \right) (-1)^{s-i} \times \\ \times \frac{d^{s-i}}{dE^{s-i}} \left[h_i(E) \left(\exp \frac{-E}{RT} \right) \right],$$

in Eqn (6) makes it possible to make sure that the former is a solution of the integral Eqn (6).

For example, for a molecule in which the number of oscillators is $s = 3$, we have

$$h(E) = h_i(E) - 2RT h'_i(E) + (RT)^2 h''_i(E).$$

Evidently the total DF is defined not only by the absolute value of the PDF but also by the $s-i$ derivatives of the functions $h_i(E)$, *i.e.* it depends on the number of oscillators in the polyatomic molecule. The reconstruction of the DF on the basis of the PDF therefore requires definite types of fitting of the experimentally measured PDF.

We shall examine specific distributions obtained on thermal heating of polyatomic molecules in shock waves. Fig. 4 presents the results of the measurements of the PDF for the CF_3I , N_2O , and CO_2 molecules obtained by absorption methods and the reconstruction of the DF on the basis of the total energy is illustrated in Fig. 5. In particular, for the CF_3I , N_2O , and CO_2 molecules, a satisfactory fit to the measured PDF is provided by the function

$$h_i = 1 - C \exp \frac{E_i}{\gamma},$$

where C and γ are the constants determined in the fitting process.

The examples presented indicate the scale of the ‘depletion’ of the DF in the vicinity of the chemical reaction barriers. Further analysis of the DF within the framework of the solution of the fundamental microkinetic equation (FME) makes it possible to obtain quantitative information about the mechanism of the activation of a highly excited polyatomic molecule and about its reactivity.

[‡] This hypothesis is valid for energy levels higher than the barrier to the state where the vibrational energy becomes stochastic.

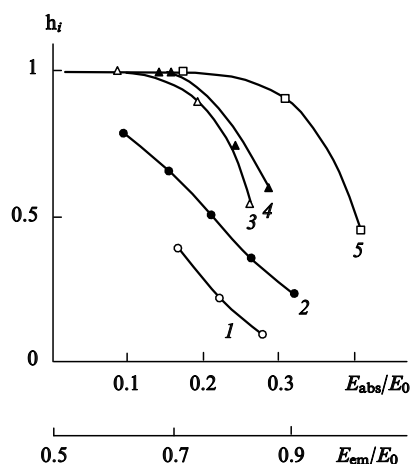


Figure 4. Dimensionless PDF with respect to the vibrational excitation energy of molecular states in reactions behind shock waves: (1) SO₂; (2) NO₂; (3) CF₃I; (4) CO₂; (5) N₂O; E₀ — reaction barrier; E_{abs} and E_{em} — excitation energies of the optically differentiated degrees of freedom measured by absorption and emission methods respectively.

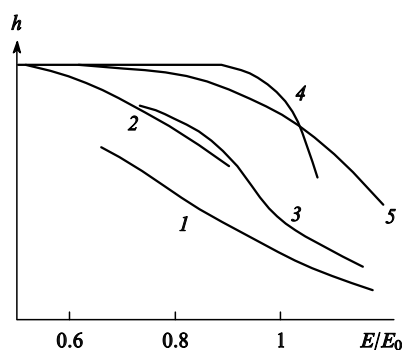


Figure 5. Dimensionless DF with respect to total vibrational energy E obtained from the PDF (Fig. 4): (1) NO₂; (2) CO₂; (3) SO₂; (4) CF₃I; (5) N₂O.

V. Fundamental microkinetic equation

For reactions occurring under thermal conditions and also for the majority of processes with laser excitation, the use of balance equations for the energy-averaged quantities is justified — for example in the case of the DF for species with respect to states having a fixed energy E between which repeated rapid transitions take place during the characteristic energy exchange time. When account is taken of the energy exchange processes, chemical reactions, and energy sources (sinks), the corresponding fundamental microkinetic equation assumes the form^{4,6,7}

$$\frac{d[A(E)]}{dt} = [M] \int_0^\infty z(E')P(E|E')[A(E')]dE' - \left[z(E)[M] + \sum_i w_i(E) \right] [A(E)]. \quad (8)$$

Here $[A(E)]$ and $[A(E')]$ are the populations of the molecules A at the levels E and E' respectively, $[M]$ is the overall concentration of species, $z(E)$ and $z(E')$ are the rate constants for the binary collisions when the energies of the molecule are E and E' respectively, $P(E|E')$ is the probability of the transition of the k th species in unit time from the state with the energy E' to the state with the energy E [the kernel of the integrodifferential equation (8)], and $w_i(E)$ is the specific rate constant for the

'external' energy sources at the energy level E . The real distribution function $f(E)$, which in the general case is different from the Boltzmann function as a consequence of the occurrence of the reaction, is defined by the relation

$$f(E) = \frac{[A(E)]}{\int_0^\infty [A(E)]dE}.$$

An important factor in the solution of the FME is the choice of a successful compromise between the physical justification of the model for the kernel of the integral equation $P(E|E')$ and the 'mathematical convenience' in the solution of the FME with the selected kernel.

The most frequently employed characteristic of the energy exchange is the average portion of energy $\langle \Delta E \rangle$ transferred per collisions, which is linked to the kernel $P(E|E')$ by the equation

$$\langle \Delta E(E) \rangle = \frac{\int_0^\infty (E' - E)P(E'|E)dE'}{\int_0^\infty P(E'|E)dE'}. \quad (9)$$

We shall examine the most widely employed functional representations of the kernel $P(E|E')$.

1. Principal models for transition probabilities

a. Exponential model

Within the framework of the exponential model, the kernel assumes the form

$$P_d(E'|E) = \exp\left(-\frac{E' - E}{\alpha_e}\right), \quad 0 < E \leq E'.$$

Here the subscript d means that downward transitions on the energy scale are considered and α_e is a parameter characterising the 'half-width' of the kernel. The transition probabilities in the upward (P_u) and downward (P_d) collisions on the energy scale are linked by the detailed balance relation

$$P_u(E|E') = P_d(E|E') \frac{\rho(E')}{\rho(E)} \exp\left(-\frac{E - E'}{RT}\right),$$

where $\rho(E)$ and $\rho(E')$ are the densities of states for the internal energies of the molecule E and E' respectively; they are usually specified by the Whitten–Rabinovitch formula (7).^{4,7} The dependence of α_e on the energy in Eqn (7) may be neglected. For the ratio of densities, the following approximation is employed:

$$\frac{\rho(E')}{\rho(E)} = \exp[B(E)(E' - E)].$$

For a weak energy dependence of the parameter $B(E)$, the integrals in Eqn (9) are expressed in a closed form.

b. Strong collisions

There are several equivalent definitions of the concept of 'strong collisions' (SC) itself (see, for example, Refs 2, 4 and 6). We shall deal with the following: strong collisions are those that in each collision between a molecule and the thermostat species, the equilibrium function is restored. In fact this is the zeroth approximation for the solution of Eqn (8), which makes it possible to reduce the latter to simple relations; it is then actually unnecessary to employ specific expressions for the kernel. Incidentally the latter assume the form

$$P(E|E') = \frac{\rho(E)}{Q} \exp\left(-\frac{E}{RT}\right).$$

Strong collisions as it were specify the upper limit to the rate of activation of the molecules and make it possible to introduce a specific scale for comparison with experimental data. The so called collision effectiveness is then introduced:

$$\beta_c = \frac{k_{d,0}}{k_{d,0}^{sc}},$$

where $k_{d,0}$ is the measured rate constant for unimolecular decomposition (or recombination) at the low pressure limit and $k_{d,0}^{sc}$ is the same quantity calculated in terms of the strong collision approximation. The analysis of experimental β_c data and also of the relation between β_c and $\langle \Delta E \rangle$ and the effective energy exchange cross-section σ_E may be found in a number of communications.^{4, 6, 7, 14}

c. The statistical energy-exchange model

The statistical energy-exchange model for transition probabilities has a clear cut physical justification and is based on the assumption of a 'collision' complex between the excited molecule A and the thermostat species M during the existence of which a statistical mixing of the energy in the complex takes place. The specific form of the kernel is unduly cumbersome even when simplifying assumptions are made^{6, 51} and we shall therefore not quote it. The statistical model has an upper limit to the portion of energy transferred.

The local-statistical activation model,⁵² using the concept of the number of active oscillators participating in the energy exchange process during collisions, is a much improved version of the statistical model.^{53–55} We may note that, within the framework of the local-statistical model, $\langle \Delta E \rangle$ depends on the parameters of a specific molecule and not only on the number of oscillators.

Another approach to the solution of the FME is based on the concept of the energy spectrum of highly excited molecules in the form of a set of discrete energy levels having the appropriate statistical weight and separated from one another by an amount equal to the average portion of energy transferred in the collisions. The stepwise excitation approximation makes it possible to formulate the so called step-ladder model.

d. The step-ladder model

In this model, transitions between neighbouring levels only are considered. The quantity $\langle \Delta E \rangle$ is the principal parameter varied. The system of kinetic equations, specifying the population of the energy levels, is formulated as follows:

$$\begin{aligned} \frac{d[A_i]}{dt} = & \sum_j W(i,j) - \sum_i W(j,i) - \\ & - \sum_i W(i) - \sum_j W_{E-V}(i), \end{aligned} \quad (10)$$

where $[A_i]$ is the population of the energy level i , $W(i,j)$ and $W(j,i)$ are respectively the rates of activation and deactivation of the level i [the designation (i,j) will be understood as transition from the level j to the level i], $W(i)$ is the term taking into account the occurrence of bimolecular reactions and of spontaneous decomposition (for levels lying above the chemical reaction barriers), and $W_{E-V}(i)$ is the rate of transition between the ground and electronically excited terms (for molecules in which there is an 'inserted' electronically excited term).

Since transitions only between neighbouring levels are postulated, the sums in Eqn (10) consist of only two components:

$$\sum_i W(i,j) = k(i,j)[M][A_{i-1}] + k(i,j+1)[M][A_{i+1}],$$

where $k(i,j)$ is the rate constant for the activation of the level i on transition of the molecule from the level j .

The step-ladder model with allowance for chemical reactions and $E-V$ exchange has been examined in detail by Gaiduchenya *et al.*,⁵⁶ who give, in particular, the energy dependence of the rate constants in Eqn (10) and provide for the possibility of the independent variation of $\langle \Delta E \rangle$ for the ground and electronically excited terms. The authors⁵⁶ solved Eqns (10) by the numerical method proposed in Kalitkin's study.⁵⁷

e. Bimodal exponential model

The bimodal exponential model may be regarded as the reasonable expansion of the simple exponential model in order to take into account explicitly the contribution of two types of collisions with transfer of large and small portions of energy.^{58–61} Analytical relations between the principal parameters of the model have been obtained^{62, 63} in a form analogous to that employed for the simple exponential model.

f. Stochastic modelling

The main advantage of the stochastic model is that it is free from *a priori* assumptions about the functional form of the kernel of the transition probabilities and can be applied with equal success to small and large polyatomic molecules and also to clusters.⁶⁴

g. Weak collisions and the diffusion approximation

In the weak collision limit $\langle \Delta E \rangle/kT \ll 1$, the fundamental kinetic equation (8) is converted into the diffusion equation on the energy scale, for which exact solutions are known. This factor, in particular, has led to the fairly considerable popularity of this approximation. Troe and coworkers,¹⁴ in whose studies the approximation apparently worked satisfactorily, also increased the number of adherents to the weak collision model.

2. Experimental data on the functional form of the kernel $P(E'|E)$

We may note that until recently the exponential model has been the most widely employed. The advantages of this model are its clarity, the possibility of obtaining a solution of the FME in an analytical form, and also the fact that the functional form of $P(E'|E)$ for certain polyatomic molecules is confirmed in broad outline by experimental facts. Direct confirmation of the adequacy of the exponential model has been obtained for the NO₂ molecule in experiments with molecular beams.⁶⁵ In these beams, one of the colliding partners is excited before collision by a laser into the energy region below the dissociation barrier. The probability of a collision jump to the dissociated state, the energy of which is higher than the given barrier, is well described by an exponential relation.

The data of Sanov *et al.*⁶⁵ 'face' the theory also with the more general question of the differentiation of the principal factors which permit the wide scale application of simple exponential relations for energy transitions in various relaxation processes: vibrational–vibrational ($V-V$), vibrational–rotational ($V-R$), and rotational–translational ($R-T$).

The question arises to what extent the above experimental data⁶⁵ may be interpreted within the framework of the more general biexponential model. The results of Sanov *et al.*⁶⁵ and the measurements of $\langle \Delta E \rangle$ based on the emission from NO₂ in shock waves are compared below.

The statistical and collision-statistical energy-exchange models are physically most justified. Other models are employed much more rarely. In most studies, it is emphasised that, in the description of the unimolecular decomposition rate constants (at least in the quasi-stationary approximation), the results of calculations are little sensitive to the functional form of the kernel [see Eqn (8)], but depend on the effective half-width of the kernel — $\langle \Delta E \rangle$. The situation for a nonstationary process is somewhat different. It has been shown⁶⁶ that the incubation characteristics of the decomposition of the N₂O molecule are described quite well

when an exponential kernel with parameters depending on the excitation energy is used.

The diversity of the forms of kernels employed makes it possible to estimate different aspects of the energy exchange processes with participation of HES and to identify the main ones among them when the results of the solution of the FME are compared with experimental data. A reasonable degree of specification of details in the description of the energy exchange involving HES, which is determined by the information content of the experiment, may be established in such a comparison.

Since the choice of a particular model is fairly arbitrary, it is essential to bear in mind certain fundamental limitations of each of them. Thus the statistical model clearly yields an upper limit to the transferred energies, while the step-ladder model fixes a portion of $\langle \Delta E \rangle$ fairly arbitrarily which sometimes requires additional analysis.

A multiplicity of publications have been devoted to the problem of the description of kinetic transformations with participation of HES on the basis of the solution of the FME. Almost all studies deal with the description with the aid of the FME of the results of measurements of the rate constants for chemical reactions with thermal, chemical, and optical activation.

A satisfactory agreement with experiment can be attained within the framework of different energy-exchange models, because the macroscopic rate constants are little sensitive to the level of specification of details in the description of the behaviour of excited states at a microscopic level. Formally this is associated with the fact that the macroscopic rate constant is determined as the result of the averaging of the microscopic rate constant $k(E)$ with respect to the distribution function:

$$k_{\text{macro}} = \int_{E_0}^{\infty} k(E)f(E)dE,$$

where $k(E)$ is the specific rate constant, which depends on the excitation energy E . Clearly, analysis of the directly observed characteristics of the functions $f(E)$ can yield significantly more information about processes with participation of HES.

VI. Steady state distributions of the populations of highly excited states for unimolecular decomposition and bimolecular reactions

We shall consider the characteristic features of the DF in reactions behind shock waves. In the process involving the decomposition of molecules after rapid heating in the shock wave, it is possible to identify two stages — rapid (on thermal excitation in shock waves; its characteristic duration is $\sim 0.5 - 10 \mu\text{s}$; under the conditions of multiphoton laser IR excitation, the duration is $\sim 10^{-8} \text{ s}$), associated with activation processes before the HES chemical reactions barriers, and slow, due to the decomposition of the molecules proper. In the course of the second stage, the DF may be regarded as steady state in terms of energy levels. In this case, the right hand side of Eqn (8) is set equal to zero. It is easy to note that the form of the steady state DF depends only on the ratio of the rate constants for the chemical reaction and the deactivation process.

The CF_3I molecule proved to be one of the most convenient objects for the investigation of processes involving HES with an energy close to that of the barrier to unimolecular decomposition at the C–I bond. We shall specify two approaches to the interpretation of the results of absorption measurements. The first, developed by Dalidchik and coworkers,^{34,45} is based on the use of ‘hot’ absorption bands in order to reconstruct the steady state HES distribution using the procedures described above for the transition from the partial distribution function with respect to the C–I bond to the distribution with respect to the total vibrational energy. The results are presented in Fig. 4.

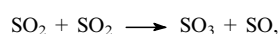
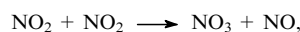
In the second approach, examined by Abel and Herzog,⁶⁷ the changes in absorption in the ‘hot’ bands after the laser pulse excitation of the CF_3I molecule are recorded. The aim of the experiments of this kind was to find, by comparing the absorption at different wavelengths, the rate of the spontaneous decomposition of HES with an energy higher than that of the decomposition barrier and then to compare the results of the measurements with calculations based on the RRKM theory. The interpretation of the measurements is difficult owing to the presence of ‘cold’ and ‘hot’ ensembles of CF_3I molecules and the influence of collisions.

1. Triatomic molecules

In the study of triatomic molecules, the experiments were carried out with NO_2 , N_2O , SO_2 , CO_2 and O_3 . The NO_2 and SO_2 molecules are particularly convenient for spectroscopic observations. Firstly, they have an excited electronic term ‘inserted’ in the ground state. The term is in quasi-equilibrium with high vibrational levels of the ground state. This makes it possible to carry out measurements based on both ‘hot’ absorption bands and on the emission in the UV and visible regions of the spectrum.^{45,49}

Reliable results of measurements of the rate of relaxation at the lowest vibrational levels as a function of temperature and the collision partners as well as data on the relaxation of the HES make it possible to ‘construct’ a full picture of the energy exchange from the ‘bottom’ of the potential well to the states above the barrier, including $E - V$ transitions.

Secondly, bimolecular reactions with activation energies significantly lower than the decomposition barriers have been investigated for the NO_2 and SO_2 molecules. We may recall that the question of the role of the vibrational excitation of molecules in overcoming the bimolecular reaction barrier is still far from being solved. Analysis of the experimentally observed depletion of the distribution of the populations of the energy levels in the vicinity of the barriers to the bimolecular reactions

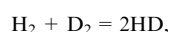


therefore yields data, which, when combined with the interpretation within the framework of the solution of the FME, may assist in significant progress towards the understanding of problems concerning the reactivity of highly excited molecules in collisions.

The attempts to find bimolecular exchange reactions occurring via a mechanism involving the subdivision of the process into the activation stage and the subsequent chemical stage proper have a long history, which does not lack certain dramatic features.⁶⁸



Here AB and CD are molecular reactants, M is any of the species in the mixture, including an inert partner, and AB^* is an active molecule which acquired a vibrational energy in stage (I) sufficient for chemical interaction with exchange of an atom or radical in the rearrangement process (II). The first model example



which was ineptly chosen¹⁴ for experimental studies (because of its high sensitivity to the distorting influence of impurities), to a large extent compromised the idea of the activation mechanism of bimolecular reactions.

The activation mechanism of bimolecular reactions received the first experimental confirmation in relation to reactions involving nitrogen oxides.^{69–71} The macroscopic manifestation of the state of nonequilibrium induced by the depletion of the populated states of AB^* in reaction (II) has been discovered in the form of the dependences of the observed rate constant k_{obs} on the ratio of the reacting components and on the presence of an inert diluent. By analogy with the curves for unimolecular reactions, the corre-

sponding curves for bimolecular reactions were referred to as fall-off curves. The depletion, compared with the equilibrium distribution of the HES of the reacting SO_2 and NO_2 molecules, found with the aid of spectroscopic methods in shock waves (Fig. 5), directly confirms the activation mechanism of the exchange reactions. The distribution obtained is well correlated with the macroscopic dependences of k_{obs} on the mixture composition.

A detailed discussion of all the aspects associated with the macroscopic manifestations of the state of nonequilibrium in bimolecular reactions may be found in the communications of Zaslonko and Mukoseev.^{69–71} We may note that the idea of the activation mechanism of bimolecular reactions and hence of the possibility of the manifestation of nonequilibrium effects has again begun to attract the attention of investigators in recent years.^{72–74} However, the calculations are of a purely illustrative character.

2. Iron clusters

Vlasov *et al.*⁷⁵ observed nonequilibrium effects in the high-temperature decomposition of clusters in shock waves. In particular, such effects are indicated by the fact that the temperatures of the clusters T_c and of the surrounding gas T_g may differ greatly with $T_c < T_g$. The current level of development of the spectroscopy of clusters does not allow the probing of the distribution of the HES as in the case of molecular objects. However, it has been possible to demonstrate directly by spectroscopic methods the depletion of the HES distribution for iron clusters containing thousands of atoms.

VII. The energy-exchange mechanism and experimental data

1. Trajectory calculations

Trajectory calculations belong to the class of the most effective methods for the study of the dynamics of the HES energy exchange for polyatomic molecules in collisions. Until recently, these calculations were mainly illustrative in character for several reasons. Firstly as a rule, a trial potential is employed. Secondly, such calculations are technically difficult to carry out for a sufficiently large number of trajectories and there is no clear-cut criterion separating elastic and nonelastic collisions from which the completion of energy exchange might be inferred. Thirdly, the relation between the results of trajectory calculations and calculations within the framework of the FME is not clear. Fourthly, trajectory calculations performed with a specific pair of colliding partners and the possibility of transferring the relations established to other pairs of colliding molecules constitutes a separate problem.

Only recently has it become possible to overcome to some extent the majority of these difficulties. For example, the distribution of the probabilities $P(E|E')$ over the entire energy range from 0 to 100 kcal mol⁻¹ has been found⁵⁹ with the aid of trajectory calculations for collisions of CS_2 with CO and was then used in the solution of the FME for the description of the relaxation of the initially excited molecules.

The systematic approach to the solution of the problem of the HES energy exchange must be regarded as the most productive and the qualitative features discovered^{61, 76, 77} must therefore be specified.

1. The results of trajectory calculations for the transitions in the collisions of CS_2 with CO agree well with calculations employing the biexponential model for the probabilities of transitions subject to the condition that the exponents depend linearly on the energy.

2. The solution of the FME with a biexponential function for $P(E|E')$ agrees well with the trajectory calculations.

3. The calculations employing the simple exponential model with an energy-independent characteristic magnitude of the 'energy jump' agree poorly with the trajectory calculations, but the introduction of a linear dependence of this parameter on the

energy alters the situation significantly. Calculations based on this 'improved' exponential model satisfactorily reproduce the characteristic features of the energy exchange.

4. Collisions which transfer of large portions of energy (strong collisions) make a much greater contribution to the overall energy exchange flux than the weak collisions. In other words, the contribution of the strong collisions to the average amount of energy transferred is the main one despite the fact that the fraction of such collisions is relatively small.

Trajectory calculations for small polyatomic molecules are used mainly to determine the ratio of the weak and strong collisions (in particular, the contributions of the $V-V$ and $V-R$ transitions).^{59, 76, 77} For large molecules, such calculations demonstrate the importance of multiple 'chattering' § collisions.^{77, 78}

Trajectory calculations make it possible to most fully discover the details of various mechanisms of the relaxation of the HES of polyatomic molecules in collisions. It is possible to identify four types of collisions with HES energy exchange.⁷⁹

1. Direct single collisions of a buffer gas atom with an atom of the excited molecule lasting less than 300 fs. Thus ~ 60% of the nonelastic collisions of toluene molecules and an argon atom may be classified as direct and these constitute 50% of the energy exchange flux.

2. 'Chattering' collisions, the duration of which is greater than that of the direct collisions but is shorter than that required for the complete intramolecular redistribution of τ_{rel} (IVR). During the collision, the atom, as it were, executes several jumps from one site to another at the multidimensional atom-polyatomic molecule potential. Such collisions constitute ~ 30% of all the nonelastic collisions.

3. Collisions with formation of a complex the lifetime duration of which is greater than τ_{rel} (IVR). In such a complex, the energy is distributed statistically among all the vibrational modes and the RRKM theory is applicable to the calculations. The fraction of such collisions for toluene molecules and argon atoms is very small.

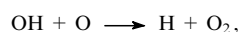
4. Supercollisions in which a very large amount of energy is transferred. However, their fraction is small, only ~ 0.1%.

The first three types of collisions may be interpreted with the aid of the modified relaxation equation taking into account the vibrational energy balance. Furthermore, equations have been obtained for $\langle \Delta E \rangle$ in various limiting cases of the energy-exchange mechanisms and the independence of $\langle \Delta E \rangle$ of temperature has also been justified.⁷⁹

One of the clearest mechanisms of the energy exchange of the HES of polyatomic molecules in collisions reduces to a sequence of $R-T$ transitions with subsequent rapid intramolecular mixing of the energy.⁸⁰ The characteristic quantity $\langle \Delta E \rangle$ for this mechanism amounts to ~ RT . The results of trajectory calculations for the collisions of SO_2 molecules and an Ar atom agree well with the results of calculations using the $V-R-T$ relaxation model. This means that the dynamics of the vibrational motion on the single collision time scale is insignificant for such calculations.

2. The influence of excited electronic terms in the HES reactions and energy exchange

In the course of the unimolecular decomposition and the reverse recombination process, species with unfilled electron shells frequently participate. Consequently one may expect the manifestation of fine structure effects. Several examples illustrating the possible scale of these effects have been examined.⁸¹ The first example refers to the reaction



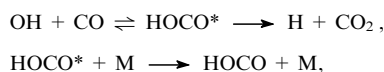
considered on the hypothesis that it proceeds within the limits of only one main potential energy surface. We then have

§ This term designates the ability of a monatomic collision partner to collide successively, several times, with several atoms of the excited polyatomic molecule.

$$k(T) = f_{\text{el},0}(T) k_0(T),$$

where $f_{\text{el},0}(T) = g_{\text{el},0}/Q_{\text{el}}(T)$ is the thermal population of the two lowest electronic states, leading to the formation of a complex, $g_{\text{el},0}$ is the statistical weight of the state, $Q_{\text{el}}(T)$ is the combined partition function of the reactants, and $k_0(T)$ is the rate constant for the reaction between species in the lowest electronic states. Experiments have shown that the decrease in the thermal population of the lowest components of the fine electronic structure of the OH radical and the O atom with increase in temperature entails a decrease in the rate of reaction, because the highest components apparently do not contribute to the reaction. Consequently the above relation for $k(T)$ has been confirmed experimentally.

The second example concerns the reaction



for which the high pressure limit (k_∞) has been found experimentally. The reaction regime at low pressures (k_0) is well known. The first stage of the reaction is determined by capture, whilst in the second stage the reverse process — the decomposition of the active complex HOCO^* — exerts an appreciable influence. If only the lowest components of the OH fine structure contribute to the reaction, then, by comparing the calculated and experimental rate constants, it is possible to find the expected contribution of the fine structure effect.

The possible influence of electronic terms on collision energy exchange processes has been tested in relation to the NO_2 molecule. The $^2B_2$ and $^2A_1$ states are known to be greatly mixed. Other electronic states, which are not linked optically, may be linked by collisions. The strong linkage between the $^2B_2$ and $^2A_1$ states promotes intramolecular exchange and, on laser excitation of molecules in the region of the dissociation barriers, the vibrational motion of the highly excited NO_2^* molecule is randomised. Apparently this in fact accounts for the absence of effects associated with the separate states for the spectrum of the products of the collision-induced dissociation.

The hypothesis of the important role of the electronic term in the NO_2 relaxation process is supported by the data of Toselli *et al.*⁸² and Hartland *et al.*⁸³ In conformity with these data, the portion of energy transferred in collisions increases sharply starting with the levels corresponding to the location of the excited term. However, measurements in crossed beams did not demonstrate the influence of this term on the energy-exchange parameters.⁶⁵ The above contradiction can be resolved only on the basis of a more detailed description of the HES relaxation.

3. Reverse electronic relaxation. $V-E$ exchange

Molecules having an electronically excited term, the 'bottom' of which lies below the dissociation barrier, are favourable objects for the investigation of energy exchange. The electronically excited states of such molecules are as a rule found to be strongly linked to the vibrational levels of the ground state (Fig. 1). However, knowing the rate of energy exchange between these states, it is possible to infer how strong this linkage is.

In the collisionless regime, the mixing of the states (the Douglas effect) greatly lengthens the radiation lifetime, for example for NO_2^* it is more than 50 μs in the vicinity of the dissociation barrier. The long lifetime of molecules in the excited state (τ) is convenient for the 'transportation' of the excitation in the molecular beam.⁶⁵ For SO_2 , this effect is most marked.

The phenomenon of the reverse electronic relaxation (RER) has been used in direct measurements of the time required for the establishment of the steady state association regime (t_{ss}) for the NO_2 and SO_2 molecules.^{56,84,85} By varying the content of SO_2 in a mixture with argon, the total pressure, temperature, and the spectral range in the recording of emission, it has been possible to identify the component associated with the $V-E$ exchange

processes in the overall time required for the attainment of the steady state dissociation regime.

The effectiveness of the RER has been estimated in relation to the resonance IR excitation process.^{12,88}

4. Vibrational relaxation of molecules in electronically excited states

The relaxation of vibrational energy within the limits of the electronically excited terms has been poorly investigated because the overall energy in these states is small and it is difficult to separate the vibrational relaxation process from the accompanying energy-exchange processes.

It has recently been possible to measure the vibrational relaxation times for the OH⁸⁹ and SO_2 ⁹⁰ molecules with the aid of laser excitation and high-resolution LIF spectroscopy. The relaxation of diatomic molecules is somewhat outside the main topic, but the situation for SO_2 merits a comment.

The rate constant for the vibrational relaxation of SO_2 within the ground term at $T = 300\text{ K}$ is $5 \times 10^{-14}\text{ cm}^3\text{ s}^{-1}$ ($\text{M} = \text{Ar}$).⁹¹ On the other hand, the relaxation within the excited term is ~ 20 times faster,⁹⁰ *i.e.* the rate of relaxation is much higher than the rate of quenching of the fluorescence of the $^3B_1(0,1,0)$, $^3B_1(0,2,0)$, and $^3B_1(1,0,0)$ states of the SO_2 molecule. We may note that the fluorescence of the $^3B_1(0,0,0)$ state is quenched 20 times more slowly. Theoretical models for the description of experimental data have not yet been developed.

5. Dependences of the relaxation of the molecular highly excited states on temperature, collision partners, and the degree of excitation

The questions raised in the heading of the present section have been almost fully resolved in relation to the relaxation of the lowest vibrational levels of small molecules, which has been reflected in the literature (see, for example, Gordiets *et al.*¹⁵).

The situation is not quite so favourable as regards the HES of polyatomic molecules, particularly since it is necessary to take into account the vibrational degrees of freedom of not only the ground but also of the electronically excited terms.

We shall now turn to the energy dependence of the rate of relaxation of the HES. There are molecules for which it is possible to construct a complete relaxation pattern from the lowest vibrational levels up to the dissociation barrier. In the first place, this applies to the NO_2 molecule, characterised by exceptionally convenient spectroscopic features. For this reason, diverse methods have been tested on this molecule.

If one is dealing with a description in terms of the language of rate constants, then the problem formulated for triatomic molecules, (including NO_2) has been solved.^{49,51} The temperature dependences of three fundamental relaxation characteristics — the decomposition rate constant at the low pressure limit and the durations of the incubation phase and relaxation via the lowest levels — have been described in the above studies within the framework of a single approach based on the solution of the FME (Fig. 6).

As regards $\langle \Delta E \rangle$, the situation is more contradictory. According to the results of a number of studies,^{69–71,86,87} the contribution of collisions with transfer of large portions of energy to the overall flux of activating collisions is notable (Table 1). Analysis of experimental data obtained in shock waves permits the following conclusions.

Firstly, in the lowest part of the energy scale the $V-T$ exchange proceeds with transfer of $600\text{--}2000\text{ cm}^{-1}$ vibrational quanta, depending on the temperature, with a probability from 10^{-2} to 10^{-3} .

Secondly, in the middle of the energy scale the portion of energy transferred $\langle \Delta E \rangle$ for NO_2 amounts to $\sim 60\text{ kJ mol}^{-1}$ (Table 1), *i.e.* is equal to $\sim 4RT$ at $T \approx 2000\text{ K}$.

Thirdly, the activation mechanism of bimolecular reactions yields β_c for the highly excited states of the NO_2^* molecule with an energy close to the bimolecular reaction barrier.

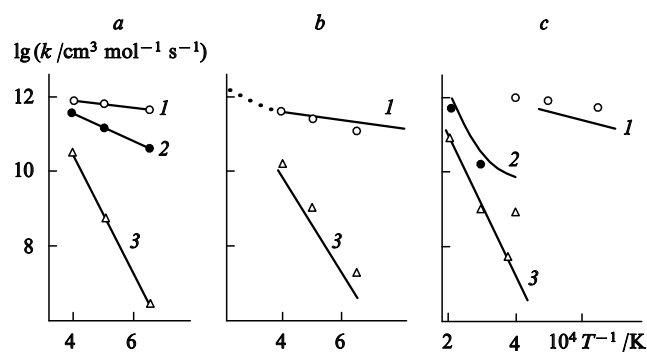


Figure 6. Experimental and calculated temperature dependences of the rate constants for various kinetic processes involving HES for the (a) NO_2 , (b) N_2O , and (c) SO_2 molecules:⁵¹ (1) relaxation rate constant; (2) incubation stage rate constant; (3) dissociation rate constant in the steady state regime; lines — fitting of experimental data in shock waves; symbols — results of the numerical solution of the FME.⁵¹

Fourthly, for transitions around the dissociation barrier there are independent β_c data in the range 0.1–0.01 ($M = \text{Ar}, \text{He}, \text{CO}_2$).⁶⁹

In the two-channel model for the parallel occurrence of bimolecular and unimolecular reactions, $\langle \Delta E \rangle \simeq RT$ and $\sigma_E/\sigma_g = 0.1$ –0.01 (see Refs 69–71 and the comments on these parameters in Refs 104 and 105).

Thus it has been possible to construct a self-consistent picture for the entire molecular vibrational energy scale on the basis of experiments employing the competing channels method and moderate-resolution emission-absorption spectroscopy.

The situation is different for data obtained by the high spectral resolution methods. Hartland *et al.*⁸³ found that the average portion of transferred energy for the NO_2 molecule is $\sim 1300 \text{ cm}^{-1}$, i.e. equal to $10 RT$ at 300 K, which agrees with the results presented in Table 1 and is also supported by measurements of the rate of V – T transitions.⁹¹ However, the results of measurements in a beam⁶⁵ yield $\langle \Delta E \rangle_{\text{up}}$ in the range of only 110–310 cm^{-1} . Furthermore, this occurs for a relative energy of

the collisions of the NO_2 molecules with Ar, He, O_2 and CO of ~ 750 – 2400 cm^{-1} .

What then is the problem? One of the causes of the discrepancies in the present author's view is the simplified interpretation of the experimental results. For instance, Pureskii⁸⁸ used for this purpose the simplest diffusion-type relaxation equation, which yields fairly good results for the upper energy scale but greatly distorts the results for relatively low excitation levels (according to the results of Zaslonko and Mukoseev,⁸⁷ in the region of the singular point).

One may postulate that the application of the exponential model for the transition probabilities will greatly improve the possibilities for the description of the primary data.⁸³ Even more interesting results may be obtained if the evolution of the DF with respect to total energy is reproduced on the basis of the observed transformation of the NO_2 high-resolution spectrum (antisymmetric vibrational spectrum). This function can then be interpreted on the basis of comparison with the solution of the nonstationary FME.

In relation to the conclusion that the activating collisions in experiments in molecular beams⁶⁵ obey the exponential model, one may assume that, for the present accuracy of the measurements, the experimental data may be fairly well described also by the biexponential model taking into account a certain hitherto unknown admixture of collisions with transfer of large portions of energy.

6. Characteristic features of the collision energy exchange of large molecules

The energy exchange in the collisions of complex molecules has been most fully investigated with the aid of the IR emission recording technique with laser pulse excitation (see the review of Barker and Toselli¹⁸).

Together with the properties characteristic of the HES of molecules with a small number of atoms, certain specific features are characteristic of polyatomic molecules.¹⁸

Firstly, the V – R energy exchange is manifested in collisions with all partners apparently by virtue of the contribution of interactions over short distances. The model of such interactions is in essence close to the model of random multiple collisions.

Table 1. Results of the measurements of the average portion of transferred energy in collisions (ΔE) and of the ratio of the energy-exchange (σ_E) and gas-kinetic (σ_{gk}) cross-sections for the lowest energy of the term (E_0) in the range of observed energies ($\langle E \rangle$).

Molecule	Term	E_0 /kJ mol ⁻¹	$\langle E \rangle$ /kJ mol ⁻¹	ΔE /kJ mol ⁻¹	T/K	$\sigma_E/\sigma_{\text{gk}}$	Excitation method
Emission measurements							
SO_2	$^1A_1$	0	360–422	39 ± 20	3600	0.01	Thermal
	$^1A_1$	0	360–422	39 ± 20	4150	0.01	"
	$^1A_1$	0	360–422	54 ± 22	2800	0.07	"
	$^1A_1$	0	380–518	30 ± 12	3600	0.02	"
	$^1B_1$	~ 334	138–263	92 ± 40	3000	0.003	"
	$^1B_1$	~ 334	138–263	84 ± 30	3300	0.004	"
	$^1A_2$	~ 334	138–184	87 ± 25	3300	0.001	"
	$^1A_2$	~ 334	25–138	88 ± 21	3300	0.01	"
	$^2B_1$	501	0–84	96 ± 25	3000	0.003	"
	$^2B_1$	~ 150	84–167	58 ± 29	1800	0.02	"
NO_2	$^2B_1$	~ 176	84–167	≥ 100	1800	0.01	"
	$^2B_2$	~ 176	84–167	≥ 63	3600	0.01	Chemical ^a
	$^2B_2$	~ 176	84–167	≥ 63	3600	0.01	Chemical ^a
Absorption measurements							
CO_2	$x \sum_g^+$	0	425–564	100 ± 45	2600	0.05	Thermal ^b
N_2O	$x^1 \sum^+$	0	242–373	50 ± 23	1700	0.006	"
CS_2	$x^1 \sum^+$	0	167–268	100 ± 31	1500	$\sim 10^{-3}$	Pulse laser ^c

^a Chemical activation method — relaxation of the HES of the NO_2 molecules formed on recombination of NO and O. ^b Thermal activation method — relaxation of the HES after heating by the shock wave. ^c Treatment of the experimental data of Heymann *et al.*¹⁰⁵

Secondly, the $V-V$ exchange occurs by virtue of the dipole--dipole interaction of the partners over large distances and the closeness to resonance between different vibrational modes is therefore significant.

Thirdly, the rate of the $V-R$ exchange increases in those cases where the molecules of the quenching gas have a permanent dipole moment, which may interact with the oscillating dipoles of the exciting molecule.

Fourthly, the presence of low-lying excited electronic terms may significantly accelerate the energy exchange.

The possibilities for the manifestation of different mechanisms of the $V-T/R$ and $V-V$ energy exchange have been examined in a study¹⁸ based mainly on the results of mode-by-mode measurements of the induced IR emission by the molecules of CO_2 used as the 'quenching' gas in collisions with the excited molecules.

Gilbert and Zare⁹² discussed the possible manifestation of quantum effects in energy exchange processes. The deactivation of the HES of azulene molecules in collisions with Ar and He was examined as an example. The appreciable difference between the effectiveness of ^3He and ^4He predicted in the above study was not confirmed experimentally.¹⁸ In contrast to the azulene--argon system, the energy exchange in the azulene--helium system is poorly described by the method of trajectory calculations apparently because of the unsuccessful choice of the potential energy surface for the given pair.

7. The possible role of supercollisions in chemical kinetics

The question of the amount of energy transferred in collisions of excited polyatomic molecules with various partners has long interested kineticists. Owing to the lack of reliable data, the majority of their theoretical studies have been carried out in terms of the approximations of strong collisions (SC) or weak collisions (WC). The controversy concerning the question which of the mechanisms is more realistic has a correspondingly long history. In many respects, the majority of investigators have been inclined to assume the dominant role of WC under the influence of the studies by Troe and coworkers (see, for example, Refs 6 and 14).

This controversy became especially intense after the observation (experimentally and by a computational procedure⁶⁰) of a significant fraction of collisions with transfer of large portions of energy. However, it had also been emphasised in earlier studies⁶⁹⁻⁷¹ that a whole series of multichannel reactions cannot be interpreted within the framework of the WC mechanism and that $\langle \Delta E \rangle$ is of the order of magnitude of RT . Since the effectiveness of the collisions β_c is much less than unity, *i.e.* the collisions can be in no way classified as purely 'strong', it became clear that it is more justified to apply the terms 'weak--strong' or 'strong--weak' collisions. Later the term 'supercollisions' (SUC) was introduced in the literature to designate the fact that in the overall energy exchange flux there is a fraction of collisions with transfer of large portions of energy.

We shall illustrate the possible role of SUC on kinetics by two examples. The first refers to the influence of SUC on the position and form of the transition curves for unimolecular decomposition reactions for a variable admixture of SUC in weak collisions.⁶⁰ Even when the fraction of SUC is 0.5%, their influence is considerable and exceeds the typical experimental errors. In view of the very common occurrence of decomposition and recombination 'transition regimes' in combustion processes and in atmospheric chemistry, much attention must be devoted to them.

The second example concerns multichannel transformations in atom-radical bimolecular reactions. The majority of such reactions occur with formation of a long-lived complex and are interpreted within the framework of the statistical theory of bimolecular reactions. The probability of a particular channel depends decisively on two parameters: the magnitude of the energy barrier for the corresponding channel and $\langle \Delta E \rangle$. In atom-radical reactions, one set of radicals is very often replaced by another set of radicals, which have different reactivities in chain

reactions. This may intensify the sensitivity of the overall reaction to the type of a particular radical by a large factor.

Model calculations have been performed^{93,94} for two-channel decompositions within the framework of the exponential energy-exchange model. However, in the light of what has been said above about the possible role of SUC, it is necessary to investigate at least the 'sensitivity' of the recommended formulae to an admixture of SUC.

8. Energy exchange in collisions with clusters

The most detailed information about the energy exchange of clusters has been obtained on the basis of the method of trajectory calculations and also the molecular dynamics method.^{95,96} The cluster is usually modelled with the aid of the Morse pair potential and the Lennard--Jones pair interaction between clusters. The results of trajectory calculations for the energy exchange of specific clusters are naturally of independent interest. However, they are still more interesting as regards the applicability of different models to the energy exchange of macromolecules and clusters in collisions. We shall differentiate the following results among those obtained:

- 1) the energy exchange parameters depend on the structure of the cluster (for a fixed mass);
- 2) the energy exchange with clusters is more effective if the vibrational frequencies are reduced; the mass of the incoming atom and the relative velocities of the partners increase.

These results are fully consistent with the predictions based on Machan's pulse model,⁹⁷ according to which the $T-V$ transitions are accelerated as Massey's adiabaticity parameter diminishes. The relations found for the maximum energy transferred in a collision when the impact parameter is zero are useful for estimates.

$$\Delta E_{\max} = \frac{4m_g m_a}{(m_g + m_a)^2} E_{\text{rel}}.$$

In the above relation m_g is the mass of the buffer gas atom and m_a is the mass of each of the atoms constituting the macromolecules m_M . The equation is most accurate for $m_a \ll m_M$ and $m_g \ll m_M$. On averaging over all possible orientations in collisions, the change in the internal energy of the cluster is

$$\langle \Delta E_{\text{int}} \rangle = \frac{\Delta E_{\max}}{2}.$$

If all other factors (*i.e.* E_{rel} and m_a) are kept constant, the energy transfer within the framework of the collision model increases with increase in m_g up to the maximum value $\langle \Delta E_{\text{int}} \rangle / E_{\text{rel}} = 0.5$ (E_{rel} is the relative translational energy of the colliding partners).

The above formulae are well supported by trajectory calculations for the collisions of Ar with Al_6 or with Al_{13} , *i.e.* $\langle \Delta E_{\text{int}} \rangle / \langle \Delta E_{\text{rel}} \rangle$ tends to 0.5 in the limit if the mass of the buffer gas atom is large, the vibrational frequencies are low, and Massey's adiabaticity parameter is small.

Estimates of $\langle \Delta E \rangle$ by the above formulae for collisions of iron clusters with an argon atom agree well with the value obtained in the theoretical description of the difference between the temperatures of the clusters and of the gas in thermal decomposition in shock waves.⁹⁸

The details of the energy exchange mechanism in the collisions of clusters with inert gas atoms have been elucidated by comparing the results of trajectory calculations with the predictions of the ergodic collision model.⁹⁶

We list below the features of such energy exchange closest to the subject of the present review.

The mechanism of energy exchange in the collisions of clusters depends on the intensity of the interaction and varies from the weak collision (WC) limit to the statistical strong collision (SC)

limit as the interaction energy varies from the scale of the van der Waals forces to values characteristic of a normal chemical bond.

For a weak interaction, the functional form of the transition probabilities in collisions $P(E|E')$ is well modelled by the relations of the partially ergodic collision theory. The functional form of $P(E|E')$ depends significantly on the parameter of the effectiveness of the collisional energy exchange β_E .

In collisions with strong interaction, a bimodal dependence of the transition probabilities $P(E|E')$ on the portion of transferred energy is observed. The central peak on this relation corresponds to weak collisions, whilst the 'wings' take into account the contribution of strong collisions.

VIII. Nonstationary distributions of the populations of highly excited states

1. The incubation phase of unimolecular decomposition reactions and the activation limit of bimolecular reactions

In the classical mechanism of a unimolecular reaction, the activation process is considered as the first stage, being followed by the chemical dissociation process proper or a rearrangement of the bonds in the activated molecule having an energy higher than the barrier to the corresponding process. For simplicity, we shall confine the treatment to the two commonest types of activation — thermal in collisions and optical in multiphoton excitation by IR irradiation (Fig. 1). Both types of activation are an example of activation 'from below'. The overall rate of the process is low up to the instant when the population of the active states of the molecules attains a steady state (not necessarily equilibrium) level. In such activation, it is necessary to pass through the entire 'ladder' of vibrational states before the barrier. In the majority of studies, the duration of this process is referred to as the incubation period and the latter is as a rule short compared with the main reaction time for an established steady state distribution function. It is more correct to call this time interval the relaxation time of the distribution function. For thermal reactions, these times approach one another with increase in temperature and conditions may be realised where the entire decomposition phase takes place as a nonstationary process and the population is small for most of the distribution function (including the region in the vicinity of the maximum). In such situations, the subdivision into incubation and steady state phases is no longer legitimate.

Naturally, the results of the measurement of the duration of the incubation phase τ_{inc} in the studies of unimolecular decomposition carry important information about energy exchange processes over the entire energy scale (from below up to the barrier). The measurement of τ_{inc} for unimolecular decomposition in shock waves is a difficult task. This problem has been solved sufficiently fully (with application of the emission technique for the excited electronic terms) only for triatomic molecules.^{45, 49}

The results obtained were interpreted within the framework of the solution of the FME with reference to experimental relaxation data for the lowest vibrational levels (Fig. 6).

The theoretical calculations for the incubation phase in a collisionless dissociation process induced by resonance IR radiation have been carried out by Troe.⁹⁹ The durations of the incubation and steady state phases for this process are comparable and, if no account is taken of this fact, misunderstandings may arise when the results obtained by different workers for the rate constants and the product yields are compared. Comparison with the results of measurements of macroscopic rate constants is valid only when the form of the distribution function with respect to the internal energy of the reactants is the same!

Despite the fact that the duration τ_{inc} is in essence a characteristic of an integral process, the interpretation of the τ_{inc} yielded interesting results for the energy dependence, the rate of relaxation as a function of the degree of vibrational excitation of the molecule.⁶⁶

A detailed analysis of studies on the incubation characteristics τ_{inc} of unimolecular decomposition reactions with thermal activa-

tion in the gas and as a result of collisions on the wall has been carried out.⁵⁰ In particular, the deficiencies of the calculations of τ_{inc} within the framework of the simplest exponential model with energy independent energy exchange parameters have been noted. These deficiencies have been overcome in other studies.^{49, 51}

2. Transformation of the distribution of highly excited states

The modelling of kinetic processes involving HES has shown that measurements of only the integral parameters of the relaxation processes in chemical reactions and also of the steady state distribution functions are insufficient for the elucidation of the detailed mechanism of the energy exchange and reactions of highly excited molecules. The problem of the diagnostics of nonstationary distribution functions and of securing information about kinetic parameters involving highly excited molecules at a microscopic level therefore arises. Owing to the limited possibilities of the recording apparatus and a lack of satisfactory theoretical models, there has been little development of this field of study hitherto.

Detailed information about the energy-exchange processes can be obtained by creating a significantly nonequilibrium initial situation and by observing the subsequent transformation of the distribution function for a polyatomic molecule as a result of collisions with thermostat species. In this case, the average energy of the polyatomic molecules should differ greatly from the average energy of the thermostat species. Such situations occur in the laser excitation of molecules (the molecules are 'cooled' in the collision process) and also on thermal excitation of the molecules in shock waves (the molecules are 'heated' as a result of collisions).

There have been fairly numerous communications whose authors investigated the transformation of the initial distribution functions having a sharp maximum in the region of high energies. Such a 'narrow' distribution is generated as a result of chemical or optical pumping. The method employing intramolecular conversion, accompanying the absorption of a laser photon in the UV or visible region of the spectrum (Fig. 7), has come to be most widely used for the generation of 'narrow' HES distributions. The advantages of this method have been clearly demonstrated in

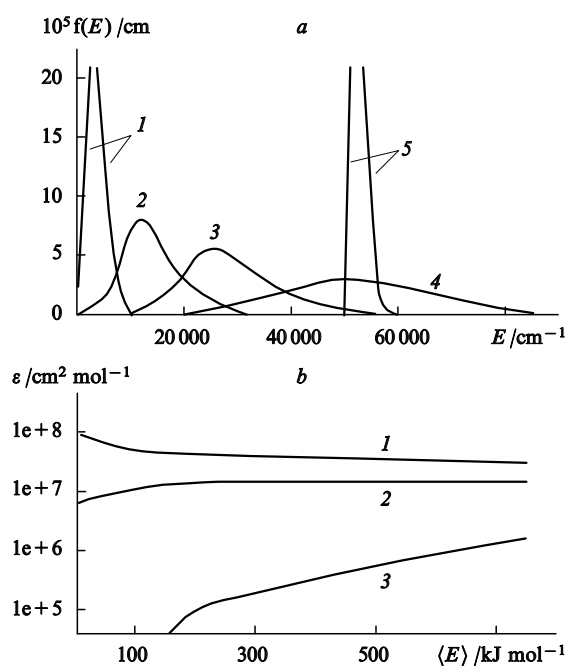


Figure 7. Transformation of the population distribution function on laser pulse excitation (a) and the dependence of the absorption coefficient of cycloheptatriene molecules on the wavelength and excitation energy $\langle E \rangle$ (b):¹⁴ a: T/K : (1) 600; (2) 1200; (3) 1800; (4) 2800; (5) 300; b: λ/nm : (1) 180; (2) 200; (3) 250.

relation to a family of substituted cycloheptatrienes, CS₂, SO₂, CrOCl₂, azulene, *etc.*^{100–104} The primary absorption step with subsequent rapid intramolecular conversion makes it possible to generate a microcanonical HES distribution within the limits of the ground electronic state. The electronic transition in the UV region is due to the optically active vibration of the polyatomic molecule, while the remaining vibrational modes play the role of an intramolecular thermostat. The vibrational energy at the $E_{\text{int}} \simeq \hbar\nu$ level becomes stochastic in a picosecond time interval. A significant advantage of this method is a clear-cut energetic definition of the initially generated distribution of molecules with respect to the total energy.

It has been concluded¹⁴ that the relaxation of the average energy of the molecules may be described by the simple equation

$$-\frac{d\langle E(t) \rangle}{dt} \simeq z(\langle E \rangle) \langle \Delta E(E) \rangle, \quad (11)$$

where $z(\langle E \rangle)$ is the number of collisions of a ‘hot molecule’ having an energy $\langle E \rangle$ with the thermostat species. This relation is of the usual kind and has been used to interpret the primary experimental data for the relaxation of HES with UV laser excitation of the molecules. In order to be able to apply this relaxation equation, it is necessary to measure the average energy $\langle E \rangle$ of the molecule. This can be done by employing UV absorption spectroscopic,^{48, 49} IR fluorescence, and IR absorption^{12, 13} methods. Almost all investigators calibrate the measuring absorption channel if the distribution function with respect to the internal energy is known; for example, in terms of the empirical experimental dependence of the absorption cross-section of the molecule on the average store of the total energy ($\langle E \rangle$) (Fig. 7). The spectra of polyatomic molecules under equilibrium conditions (a canonical distribution of the molecules with respect to internal energy) and with UV laser excitation (a microcanonical distribution) are virtually the same, provided that the average energies of these ensembles are identical.¹⁴ For the triatomic SO₂ and CS₂ molecules, the calibration is less satisfactory.¹⁰⁵

The possibility of selecting a suitable wavelength in the UV absorption spectrum, for which an unambiguous relation between the absorption cross-section $\sigma(t)$ and the average energy of the molecules holds, has been justified.^{67, 103, 104} Subsequently the kinetic absorption curve is transformed with the aid of the $\sigma(\langle E \rangle)$ relation into the $\langle E \rangle(t)$ relation, which is in fact used in Eqn (11). The cross-section of the deactivation process is then assumed equal to the gas-kinetic cross-section. As a result, the values of $\langle E \rangle$ for collisions with inert monatomic gases in the region of $(0.01 - 0.001) RT$ are obtained for CS₂ and SO₂ in the lower part of the potential well, which is frequently even less than the energy of the rotational quanta of the molecule. This agrees poorly with the overall picture of the vibrational relaxation of polyatomic molecules.

The above conclusions are a consequence of the limited applicability of the initial postulates underlying the interpretation of the experimental data. Firstly, analysis of the fundamental kinetic equation, carried out by Zaslonko and Mukoseev,⁸⁷ showed that Eqn (11) has a limited applicability. It is valid only for systems without vibrational energy sources or sinks as a result of the occurrence of chemical reactions of the HES and also for excitation energies significantly higher than the level of the average thermal energy of the thermostat molecules and subject to the condition that $\langle \Delta E \rangle \ll E$. In particular, neglect of this important factor (see Nikitin¹⁴ and the literature quoted therein) led to a strong dependence of $\langle \Delta E \rangle$ on the excitation energy (or, what amounts to the same thing in the context of the above study, a strong temperature dependence of $\langle \Delta E \rangle$).

Secondly, the dependence of the absorption cross-section on the average energy of the molecules is not universal and for certain wavelengths may depend on the form of the distribution function and hence on the external conditions governing the activation of molecules.

3. Wave characteristics of the transformation of the distribution of populations on pulse excitation

We shall now consider the results of the analysis of the properties of the system of microkinetic equations for the population of the highly excited states of polyatomic molecules with pulse excitation. A generalised FME has been obtained^{86, 87} for the dimensionless distribution function of the populations in the presence of sources and sinks of excited states. With the aid of this equation, it is possible to find the correct limiting transitions to special cases of activation in the diffusion approximation and via the strong collision mechanism.

A fundamental feature of the analysis is the identification of singular points of the kinetic system, described within the framework of the FME, separating different dynamic energy-exchange process regimes. Depending on the energy function of the activation cross-section in collisions, the singular point is determined either by the average energy transferred in the collision $\langle \Delta E \rangle$ or by the average thermal energy of the species in the ensemble sRT , where s is the number of oscillators in the molecule. In the vicinity of the singular point, the energy-exchange kinetics can be satisfactorily described by a diffusion mechanism. Under conditions far from the singular points in the region of energies $E > \max\{\langle \Delta E \rangle, sRT\}$, the solution of the generalised FME is expressed in the form of a population travelling wave. The clearest results are obtained when the method of characteristics is employed. In the coordinate system linked to the moving population front, the solution has an exponential form with a characteristic region of the population gradient, which depends on $\langle \Delta E \rangle$. Under conditions far from the sources and sinks of the excited states and also for $E \gg \langle \Delta E \rangle$, the rate of movement of the population front is constant and only then can be fitted by the simple equation

$$\frac{dE}{dt} = \langle \Delta E \rangle k_i^{(+,-)},$$

where $k_i^{(+,-)}$ are the rate constants for activation or deactivation and the ‘plus’ or ‘minus’ sign denotes the direction of motion of the population front, which depends on the initial conditions. In the absence of an energy dependence of $\langle \Delta E \rangle$ and $k_i^{(+,-)}$ the movement of the population front is of the automodel type: its form is retained and there is no dispersion in the distribution. When the population front approaches the barrier to the spontaneous decomposition of the excited molecules, the wave is retarded (there is a dispersion in the distribution) (Fig. 8).⁸⁷

The above analysis provided a basis for a new method whereby the parameters of the energy exchange of highly excited states of polyatomic molecules may be determined experimentally. Its essential feature reduces to the measurement of the phase and amplitude characteristics of the relaxation process and the determination of the form of the population distributions. In the simplest formulation, for the solution of the problem it is sufficient to measure simultaneously the rates of change of the absorption (emission) at two wavelengths corresponding to two energy levels of the excited states. The simplest and at the same time fairly informative parameters of the experimental kinetic curves are the induction phase related to the time of arrival of the population front at the given energy level (τ_1 and τ_2 in Fig. 9) and the rate constant for the population of the given level ($\langle \Delta E \rangle$ characterises the form of the distribution of populations and $k_i^{(+,-)}$ characterises the amplitude of the populations in the given instant).

Two methods for the spectroscopic recording of the wave characteristics of the HES relaxation in shock waves have been applied. The first involves the recording of the emission from triatomic molecules in the UV and visible regions of the spectrum. The high sensitivity and a time resolution which is record-breaking for the shock wave technique have been achieved as a result of a spatially integrated emission system along the axis of the shock wave tube. The second procedure involves the recording of the ‘hot’ absorption bands of the molecules. An important precondition

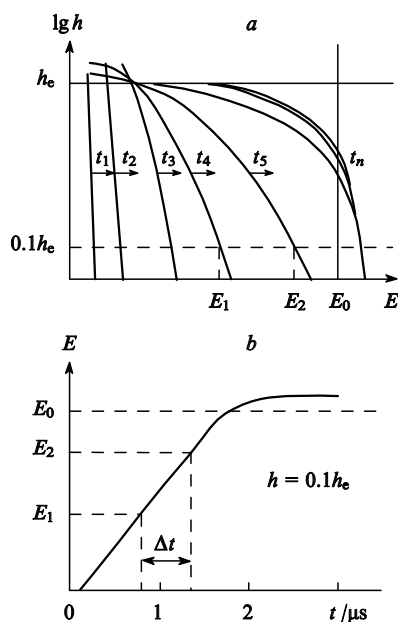


Figure 8. Examples of the numerical solution of the FME for the time evolution of the dimensionless DF, $h(E) = f(E)/f_{eq}(E)$, for vibrational energy on thermal activation in the shock wave; h_e — level of equilibrium population; E_0 — decomposition barrier; E_1 and E_2 — recorded energy levels; Δt — the time taken to traverse the population level over the specified energy range. *a*: form of DF at different times fitted by the relation $h(E) \approx e^{-\alpha E}$, where $\alpha \approx 1/\langle \Delta E \rangle$; $\Delta h(E)/[h(E)(E_2 - E_1)] = 1/\langle \Delta E \rangle$; *b*: trajectory of the motion in time of the constant-population level $0.1 h_e$ fitted by the equation $dE/dt = \langle \Delta E \rangle k_{rel}[M]$, where $(E_2 - E_1)/\Delta t = \langle \Delta E \rangle k_{rel}[M]$ and k_{rel} is the relaxation rate constant.

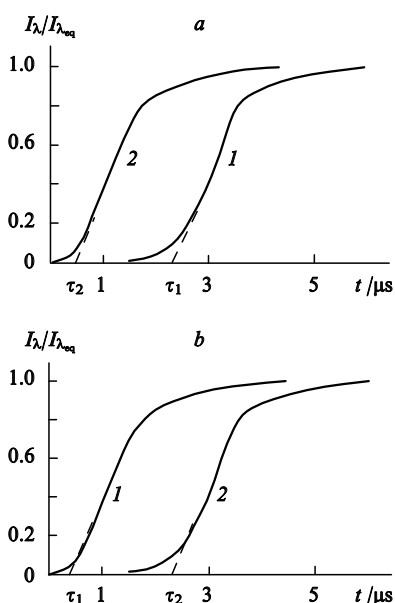


Figure 9. 'Distance traversed' by the population wave in the range of energies of NO_2 molecules of 212–240 kJ mol^{-1} (emission in shock waves): (a) relaxation 'from above' in the recombination process $O + NO \rightarrow NO_2^*$; (b): relaxation 'from below' in the collisions $NO_2 + Ar \rightarrow NO_2^* + Ar$; $\lambda(\text{nm})$: (1) 585; (2) 500; $E(\text{kJ mol}^{-1})$: (1) 210; (2) 240.

tion for the quantitative measurements is the possibility of calibrating the emission and absorption recording channels with respect to wavelength.

The measurements were performed with SO_2 , NO_2 , and CO_2 molecules.^{86,87} The temperature range of the measurements was

1800–4000 K, the pressure was 2–5 atm, the diluent gas was argon, and the fraction of the molecular component was from 0.5% to 20%. The range of vibrational excitation energies capable of being recorded amounted to 10–130 kJ mol^{-1} for the absorption method and 180–500 kJ mol^{-1} for the emission method. In all the experiments, measurements were made simultaneously at at least two wavelengths. The energy gap between the energies of the recorded excited states was as a rule 30 kJ mol^{-1} .

The selected recording scheme made it possible to determine accurately the distance traversed by the population wave for the specified energy interval (Fig. 9). Opposite directions of wave travel were observed for NO_2 molecules with shock wave heating (relaxation 'from below') and in the recombination reaction $O + NO \rightarrow NO_2$ (relaxation 'from above'). The phase shifts of the signals in the two-channel recording, caused by the difference between the induction periods τ_1 and τ_2 were in the range 0.3–6 μs , while the rate constants for the population of the highly excited states in collisions were in the range 3×10^{10} – $4 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (in an argon atmosphere). The recording of the propagation of the population waves permits the direct determination of an important energy exchange parameter — $\langle \Delta E \rangle$. The clearest estimate of $\langle \Delta E \rangle$ is obtained from the law governing the motion of the population front:

$$\frac{E_1 - E_2}{\tau} = \langle \Delta E \rangle k_i^{(+,-)},$$

where E_1 and E_2 are the energy levels of the recorded excited states. We emphasise that this approach to the determination of $\langle \Delta E \rangle$ does not employ any additional (as a rule arbitrary) hypotheses concerning the energy-exchange mechanism.

The interpretation of the emission and absorption data in shock waves made it possible to determine the quantity $\langle \Delta E \rangle$ for the SO_2 and NO_2 molecules in the ground and excited electronic states and also for the CO_2 , N_2O and CS_2 molecules in the ground states, which in all cases proved to be appreciably greater than RT , while the effective energy exchange cross-section σ_E is significantly smaller than the gas-kinetic cross-section σ_{gk} (Table 1). This result is of fundamental importance, because it provides a reliable basis for the elucidation of the real mechanism of the activation of polyatomic molecules in collisions without being restricted, as has been the usual practice hitherto in the vast majority of studies, to an arbitrary choice between two limiting mechanisms — strong collisions and the diffusional approximation. Unfortunately in the earlier determinations of $\langle \Delta E \rangle$ published previously the form of the distribution of populations during the relaxation of highly excited molecules was not monitored and in the interpretation of experimental data the authors introduced the seemingly obvious but in essence arbitrary assumption that $\sigma_E = \sigma_{gk}$.¹⁴ The results of a number of investigations^{69–71,86,87} have shown that the single-channel spectroscopic methods for the recording of the relaxation of highly excited molecules make it possible to determine only the product $\langle \Delta E \rangle \sigma_E$. For the separate determination of the multipliers, two-channel measurements with monitoring of the form of the distribution of the populations during relaxation are necessary. We may note that the spectroscopic recording of the steady state distribution of the populations of the HES of the molecules in the course of thermal decomposition behind shock waves, achieved earlier by Zaslonko and coworkers,^{45,106} also makes it possible to determine only the product $\langle \Delta E \rangle \sigma_E$.

The recording of the nonstationary distributions of the populations of the HES of molecules during relaxation is free from the disadvantages noted above and permits the separate determination of $\langle \Delta E \rangle$ and σ_E . Evidently the application of high-resolution spectroscopy is promising for the monitoring of the distribution function in the course of the relaxation of the HES in collisions. This has been most strikingly demonstrated in relation to the NO_2 molecule: a Fourier spectrometer was used for the recording of the IR emission spectrum of NO_2 molecules excited by a laser in the range 800–10 000 cm^{-1} with a spectral reso-

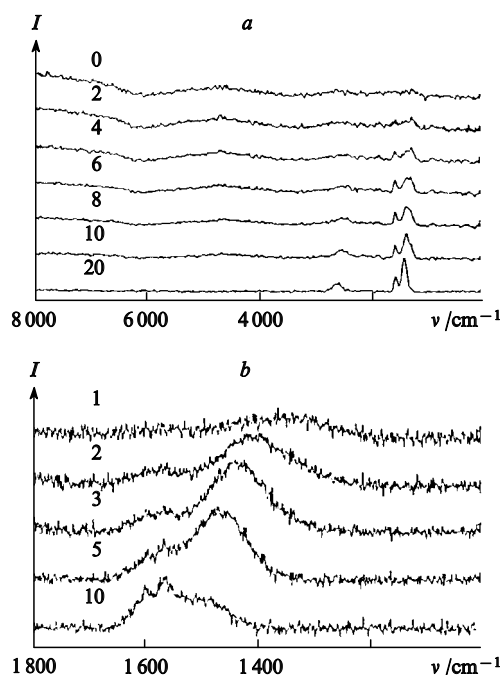


Figure 10. Transformation of the emission spectrum of the NO_2 molecule after excitation by a pulse laser.⁸³ Recording by the time-resolved Fourier transformation method. Resolution 1 cm^{-1} ; NO_2 pressure 1.7 Torr. The numerals against the spectra represent the time interval (μs) after the laser pulse up to the start of the measurement.

lution of 1 cm^{-1} and a time resolution of $0.5 \mu\text{s}$.⁸³ These are indeed excellent apparatus parameters and they led to impressive results. It was possible to measure the energy dependence of $\langle \Delta E \rangle$ for the $\text{NO}_2^* - \text{NO}_2$ collisions (a sharp increase from $\langle \Delta E \rangle < 50 \text{ cm}^{-1}$ with $\langle E \rangle \simeq 13\,000 \text{ cm}^{-1}$ up to $\langle \Delta E \rangle \simeq 1300 \text{ cm}^{-1}$ with $\langle E \rangle \simeq 20\,000 \text{ cm}^{-1}$) and a narrowing of the HES distribution as the relaxation process proceeds (Fig. 10).

In the initial instants of the relaxation, the NO_2 bands investigated (ν_3) have undergone a 'red' shift relative to the 'normal' frequency of 1617 cm^{-1} because the initial part of the emission signal is due to the emission from high levels with pronounced anharmonicity.

Unfortunately, no attempt was made⁸³ to relate the observed spectrum in the narrow frequency range to the total vibrational energy of the molecules and the simplest relaxation equation was used for the interpretation of the results of this study. We suggest that appreciably more information may be extracted from these data⁸³ on the basis of the description of the HES relaxation in the travelling population wave regime (see above).

This is well illustrated by the treatment of the primary experimental data on absorption in the 'hot' bands of the highly excited CS_2 molecules, such bands being generated on laser pulse excitation in the form of an initial δ -distribution (Figs 7 and 11).¹⁰³ If the shift of the absorption band observed in two-channel recording is ignored and they are treated by the single-channel method, as was done by Hippler *et al.*,¹⁰³ then the values of $\langle \Delta E \rangle$ obtained for the 'bottom' of the potential well are found to be very low. However, the observed shift of the absorption curves indicates the wave character of the propagation of the population wave. The values of $\langle \Delta E \rangle$ found agree well with the results for the SO_2 , NO_2 , CO_2 , and N_2O molecules in shock waves (Table 1).

The average values of $\langle \Delta E \rangle$ and σ_E obtained by Zaslonko and Mukoseev⁸⁷ lead to the possibility of solving the problem of the reconstruction of the real functional form of the energy dependence of the transition probability $P(E|E')$ in collisions and also demonstrate the presence of an appreciable fraction of collisions

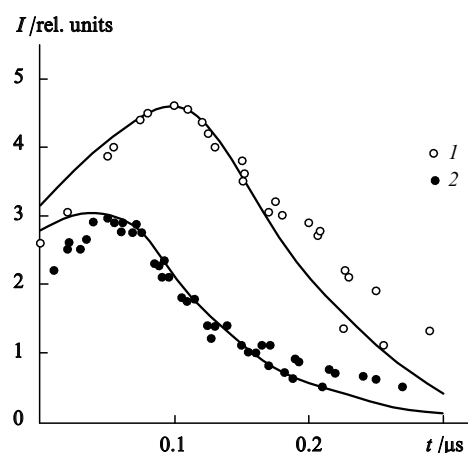


Figure 11. Time dependence of the absorption of light in the regions of $\lambda = 240 \text{ nm}$ (1) and 260 nm (2) by CS_2 molecules on pulse excitation by an excimer laser with an emission wavelength of 316 nm at $T = 1500 \text{ K}$. Circles — experiment;¹⁰⁵ lines — calculation based on the model developed by Zaslonko and Mukoseev;⁸⁷ agreement with experiment at $\langle \Delta E \rangle = 100 \text{ kJ mol}^{-1}$; $k_{\text{rel}} = 3 \times 10^7 \text{ s}^{-1}$.

involving transfer of large portions of energy. Recently, such collisions have attracted the attention of investigators, since their appreciable role in high-temperature chemical kinetics has been suggested.⁶⁰

IX. Intramolecular relaxation

The problem of finding the characteristic rates of the intramolecular exchange of vibrational energy arose first in the interpretation of data on the kinetics of unimolecular reactions, vibrational predissociation, and the theory of mass spectra (see Refs 4 and 9 and the literature quoted therein).

Model ideas about the nature of the intramolecular relaxation (IVR) are used in all modern theories of elementary chemical reactions. The close relation between IVR and the chemical reaction step proper is illustrated by the energy diagram for the isomerisation process (Fig. 12). The quasi-harmonic description of the vibrations in the lower parts of the potential wells of the initial molecules and products becomes inapplicable on moving to the reaction barrier and at least one of the normal vibrations degenerates into translational motion along the reaction coordi-

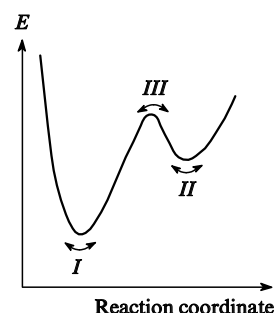


Figure 12. Energy diagram illustrating the transitions between various vibrational motion regimes in polyatomic molecules during the isomerisation process; $3n-6$ normal vibrations of the initial molecules in the region of the initial reactants (I) pass to the stochastic vibrational regime in the vicinity of the reaction barrier with degeneration of at least one vibration to translational motion along the reaction coordinate with subsequent generation of a new set of $3n-6$ normal vibrations in the region (II) of the reaction products; (III) transition region.¹⁰⁷

nate [the vibrational frequency then becomes imaginary: $\omega = (k/\mu)^{1/2}$, $k < 0$].

The current state of studies on IVR has been described in a series of reviews (see, for example, Refs 107–109). Three dynamic IVR regimes, corresponding to different levels of excitation on the potential energy diagram, are distinguished. For a low level of excitation, whereupon the IVR times are relatively long, the application of IR diagnostic methods with high spectral resolutions is especially effective. In the second more extensive intermediate range of vibrational excitation energies, the IVR kinetics are usually followed by spectroscopic methods involving high vibrational overtones and methods involving the generation of HES with the aid of stimulated emission and fluorescence spectroscopic recording. The third group of studies refers to the region of highly excited states above the thresholds of dissociation, isomerisation, *etc.* reactions.

We shall quote two examples of specific IVR results. The first illustrates the dependence of the IVR rates on the structure and/or density of the states. The measurements were performed by the IR spectroscopic method with high (0.0005 cm^{-1}) spectral resolution in relation to the C–H bond in hydrocarbon molecules cooled in an ultrasonic jet. The results for a family of R–C≡C–H molecules with different end groups are presented in Table 2.

It can be seen that the rate of IVR depends little on the nature of the substituent groups: it changes by not more than a factor of

Table 2. Characteristic IVR times for the family of substituted ethyne derivatives.¹⁰⁷

Molecule	τ_{IVR} /ps	Density of vibrational spectrum /No. of states per cm^{-1}
$\text{CH}_2(\text{OH})-\text{C}\equiv\text{CH}$	500	20
$\text{HC}\equiv\text{CCH}_2\text{CH}_3$	270	22
$(\text{CH}_3)_3\text{CC}\equiv\text{CH}$	200	490
<i>gauche</i> - $\text{CH}\equiv\text{CC}(\text{CH}_3)_2\text{H}$	240	2400
<i>trans</i> - $\text{CH}\equiv\text{CC}(\text{CH}_3)_2\text{H}$	440	2400
$(\text{CD}_3)_3\text{CC}\equiv\text{CH}$	40	2800
$(\text{CF}_3)_3\text{CC}\equiv\text{CH}$	60	10^{11}

two when the density of states varies by ~ 2 orders of magnitude. The decrease in τ_{IVR} by approximately an order of magnitude is observed only for fluoro-substituted derivatives when the density of the vibrational spectrum increases by seven orders of magnitude.

The second example refers to the competition between IVR and predissociation. An interesting scheme for observations of this phenomena has been used for weakly bound clusters where even the excitation of the ground state in the near IR yields an excitation energy which is higher than the bond strength. Fig. 13 presents the measured and calculated spectra of the ν_5 antisymmetric DF stretching vibration in the trimer $(\text{DF})_3$ with hydrogen bonds.¹¹⁰ The average band contour corresponds to a D_{3h} cyclic structure. Fine structure, corresponding to a much denser spectrum (a difference by three orders of magnitude) than expected for a rigid molecule at 10 K can also be seen. This spectrum corresponds to the DF vibration with ring modes in the presence of mixing of various structures as a result of IVR. Mixing of this kind ensures an excitation energy sufficient to dissociate one hydrogen bond in the ring and to form the entropically more favourable flexible linear isomer, the characteristic time of the transition being ~ 40 ps. The opening of the trimer ring, which also corresponds to the dissociation of hydrogen bonds, is 10–100 times faster than the predissociation in the DF dimer. Such a large

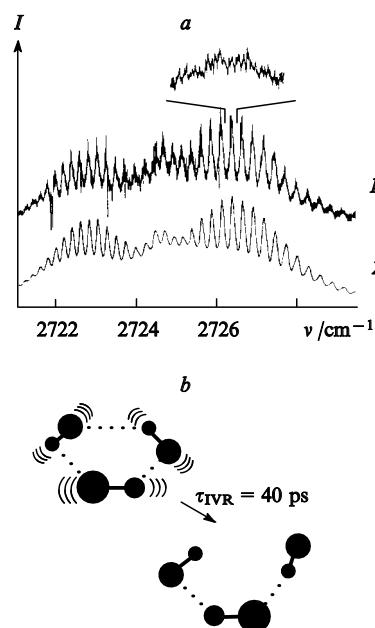


Figure 13. High-resolution IR spectrum in the region of the antisymmetric DF vibration in the $(\text{DF})_3$ trimer formed on cooling in an ultrasonic jet to a temperature of 10 K (a) and schematic illustration of the transitions between two structures of the trimers with hydrogen bonds (b).¹⁰⁷ (1) experiment; (2) calculation.

difference between the rates may be associated with the influence of the strain in the ring structure on the dynamics of the dissociation of hydrogen bonds.

Interesting questions concerning the characteristic features of IVR in spaced out and dense spectra have been discussed in a number of communications (see, for example, Quack and Kutzelnigg⁹). The latest advances in the IVR theory have been described by User.¹¹¹

1. The mechanisms of intramolecular relaxation and spectroscopic data

We shall examine the results of the study of the mechanisms and rates of IVR. The presence of heavy atoms in the molecule may induce a retardation of IVR.¹¹² This phenomenon may be interpreted both within the framework of simple models of molecules of the type XY_n with identical light atoms Y and a heavy central atom X¹⁰ and within the framework of the model of local vibrational modes.^{113, 114}

In another mechanism, leading to a higher rate of IVR, the linkage between vibrational modes via a series of lower-order resonances is considered.^{115, 116}

One of the most important facts observed during the last decade is that there exists a fairly wide range of possible time scales for IVR with markedly different scales within the limits of one molecule^{117, 118} and large differences for different types of chemical groups.^{119, 120} The highly excited C–H vibrations in the alkyl and acetylenic groups may serve as a characteristic example. Vibrations have been investigated also by overtone vibrational spectroscopy for molecules ensuring a spectral resolution better than 0.1 cm^{-1} (Table 3).

The existence of internal rotations (such as those of methyl groups) also promotes a higher rate of IVR.^{22, 121}

Table 3. Intramolecular IVR relaxation times for the initial excitation of the vibration of the CH group in alkanes and ethynes.⁹

Compound	$\tau_{\text{IVR}}/\text{ps}$
Alkanes	
X_3CH ($\text{X} = \text{D}, \text{F}, \text{Cl}, \text{Br}, \text{CF}_3$)	< 0.1
XF_2CH ($\text{X} = \text{D}, \text{Cl}, \text{CF}_3$)	< 0.1
Ethyne	
$(\text{CX}_3)_3\text{CCC}=\text{CH}$ ($\nu = 1$) ^a	
$\text{X} = \text{F}$	$\geq 10-20$
$\text{X} = \text{H}$	> 200
$\text{X} = \text{D}$	≥ 40
$(\text{CH}_3)_3\text{Si}-\text{C}\equiv\text{C}-\text{H}$ ($\nu = 1$) ^a	≥ 2000
$\text{CH}_3\text{CH}_2\text{C}\equiv\text{C}-\text{H}$	> 269

^a ν = number of vibrational level.

2. The rate of intramolecular relaxation as a function of the excitation energy

For the interpretation of kinetic data on the reactions of HES of polyatomic molecules, it is important to have sufficiently accurate and at the same time simple relations suitable for estimates of the rate of IVR. This problem has been solved⁷¹ by employing the procedures of the theory of random functions. Relations were obtained for the estimation of the energy dependence of the time required for the vibrational motion to become stochastic, which agrees well with the results of trajectory calculations:

$$\tau_c \omega = (7 - 20) \frac{E_0}{\hbar \omega \nu^3},$$

(E_0 is the dissociation barrier, ω the average vibrational frequency, and ν the average number of vibrational states) and with the critical number of the average vibrational quantum ν_c for which the regular vibrational motion degenerates to random motion:

$$\nu_c = \left[\frac{64}{15} \frac{(s-1)!}{s^{s-1}} \frac{E_0}{\hbar \omega} \right]^{1/(s+2)}.$$

3. Unimolecular decomposition

The question arises whether unimolecular reactions, the kinetics of which should be interpreted outside the framework of the RRKM theory, can be observed. This question has for a long time troubled kineticists. The initial analysis of the problem was given in a communication¹²² in which the most promising formulations of experiments for the observation of deviations from RRKM kinetics were noted.

The discovery of the collision-free dissociation of polyatomic molecules on resonance IR multiphoton laser excitation and the successful highly selective separation of isotopes naturally required an adequate theoretical interpretation and the discussion concerning the limits of applicability of the statistical theory of unimolecular reactions was therefore revived (see, for example, Refs 12, 13, and 16). It was found that, at least on the time scale of a $\sim 10^{-9}$ s pulse, the RRKM theory described quite satisfactorily the kinetics of the spontaneous decomposition of active polyatomic molecules excited by a pulse from an IR laser.

Simultaneously with the development of spectroscopic methods, attempts were made to seek molecules on which one can demonstrate the nonstatistical features of the spontaneous decomposition rate constants $k(E)$, but these were unsuccessful. The constant $k(E)$ depends decisively on the rate of IVR (see above).

We may also note a novel approach, proposed for the observation of kinetic phenomena, which goes beyond the framework of the traditional RRKM theory.¹²³ This concerns the mechanism of reversible unimolecular reactions and the possibility, in principle, of determining the equilibrium canonical rate

constants at low pressures without resorting to a laborious measuring procedure and treatment of fall-off curves. It has been demonstrated on model examples using the solution of the FME that such paradoxical behaviour is realistic and methods for the corresponding observations have been noted. However, an experimental test of the ideas put forward by Quack¹²³ has not so far been carried out.

One of the latest attempts to discover deviations from the theory of unimolecular reactions on the decomposition time scale of the order of several microseconds has been made by Schlag and Levin.¹²⁴ The attempt to revise the statistical theory was stimulated by the apparently anomalously short decomposition times for large polyatomic molecules on excitation by electron impact in a mass spectrometer chamber. The authors used the classical version of the statistical theory but they introduced the hypothesis that for large polyatomic molecules the IVR process in the range of energies above the decomposition barrier does not ensure the complete mixing of the energy, as a result of which the number of effective oscillators s_{ef} is significantly smaller than the total number of oscillators $s = 3n - 6$. The large difference between s and s_{ef} is equivalent to an appreciable decrease in the lifetime of the active states of the large molecules. The question therefore arises to what extent the hypothesis that the IVR process may be so slow is valid. However, it was found that the above discrepancy between the observed and measured lifetimes of the active states of large molecules may be satisfactorily accounted for within the framework of a modified version of the statistical theory in which the vibrational temperature of the molecule has been taken into account and by calculating on this basis s_{ef} without resorting to the hypothesis that IVR is slow.¹²⁵

X. Reactions of highly excited states of polyatomic molecules

1. Spontaneous unimolecular decomposition

The first successful attempts to measure the specific rate constants $k(E)$ for the spontaneous decomposition of polyatomic molecules with an energy greater than the barrier D involved photoactivation in stationary and pulse regimes.⁶ In full conformity with the RRKM theory, the values of $k(E)$ found for the molecules of the cycloheptatriene family varied as the number of groups adjoining the main ring was altered (Fig. 14). The results of direct measurements of $k(E)$ in the decomposition of ions have been described.^{7,8}

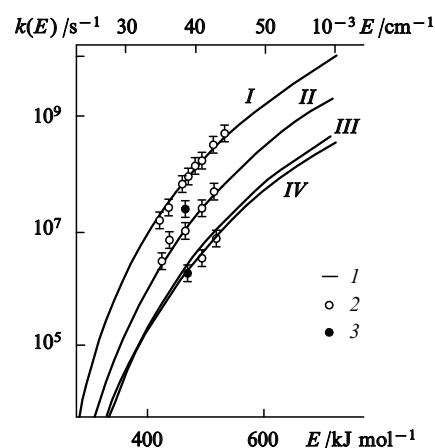


Figure 14. Energy dependence of the specific rate constants for the spontaneous decomposition of active molecules of cycloheptatriene (CHT) (I) and its methyl derivative (Me-CHT) (II) and ethyl derivative (Et-CHT) (III, IV): (I) determination from the rate constant for isomerisation $k_{\infty}(T)$ under thermal conditions at the high-pressure limit; (2) interpretation of the stationary photolysis on the basis of the Stern–Volmer curves; (3) laser pulse photolysis with recording of the evolution of the ‘hot’ absorption bands.⁷

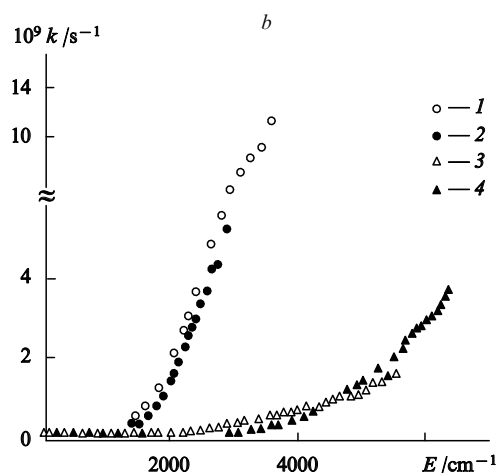
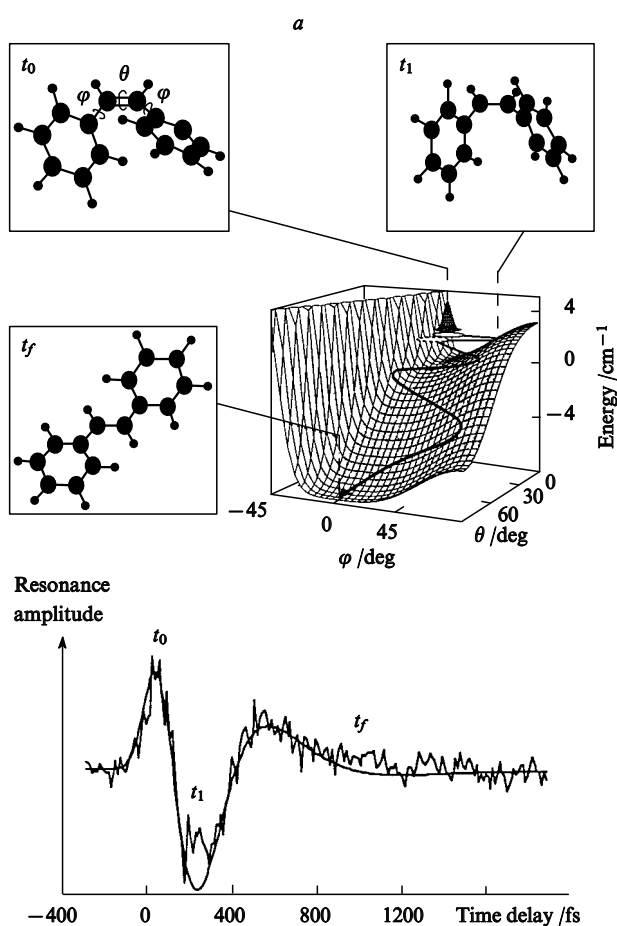


Figure 15. Femtosecond dynamics of the isomerisation of stilbene:¹²⁶ (a) transitions between different structures of stilbene and the trajectories of the motion of the representative point on the potential energy surface; (b) dependence of the rate constant for the spontaneous decomposition of stilbene (1), 4-methoxystilbene (2), 4,4'-dimethoxystilbene (3), and 2-phenylnidenestilbene (4) on, the amount by which the vibrational energy exceeds the barrier.¹²⁷

For direct measurements of $k(E)$ for reactions with neutral molecules, it is most effective to employ the following methods for the preparation of HES with a clearly defined energy state: single-photon excitation of high vibrational overtones within the limits of the ground electronic state; single-photon excitation of electronically excited states followed by rapid internal conversion to high vibrational levels of the ground state (Figs 1 and 7).

The methods based on the molecular 'hot band' spectroscopy proved entirely capable of ensuring the necessary level of sensi-

tivity and time resolution for measurements of $k(E)$. Sufficiently 'broad' HES distributions are also obtained on multiphoton IR excitation.

The results of direct measurements of $k(E)$ by various methods have been published.^{126, 127} The isomerisation reactions of stilbene (Fig. 15) and the spontaneous decomposition of NCNO molecules by ultrashort laser pulses (Fig. 16) have been examined. The manifestation of threshold effects for isomerisation and appre-

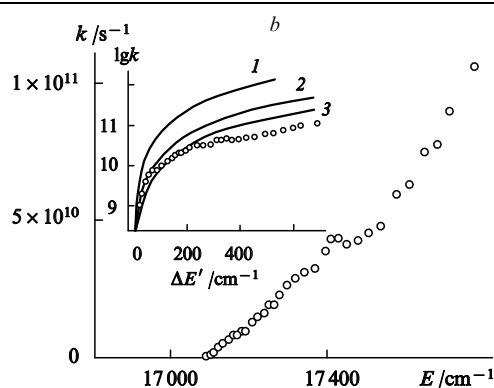
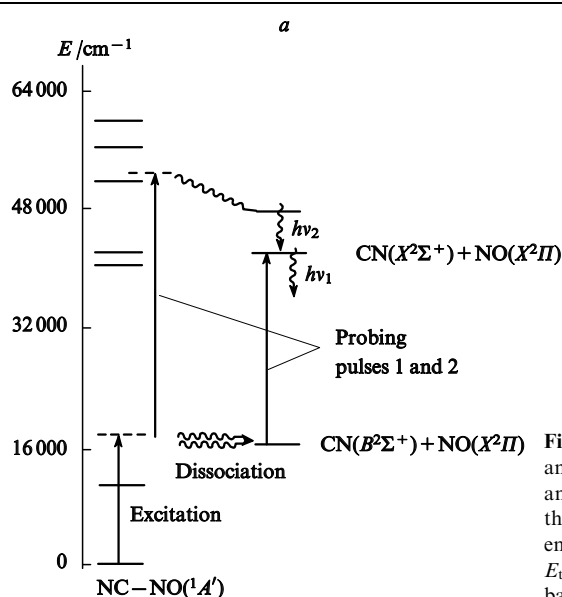


Figure 16. Energy diagram for the transitions on laser excitation of NCNO molecules and the spontaneous decomposition of NCNO* molecules excited by a laser pulse to an energy region above the spontaneous decomposition barrier (a) and dependence of the spontaneous decomposition rate constant on the amount by which the vibrational energy of the NCNO* molecules exceeds the decomposition barrier $E_{\text{th}} = 17083 \text{ cm}^{-1}$ (b).¹²⁷ Results of theoretical calculations of $k(E)$: (1) calculation based on the canonical theory of the reaction phase space; (2) and (3) calculation using modified versions of the statistical theory; circles — experimental data.

cial changes in the position of the barrier and in the rates of isomerisation as a function of structure can be seen in Fig. 15.

2. Bimolecular reactions of highly excited molecules

The characteristic features of bimolecular reactions of diatomic and polyatomic molecules with a moderately high vibrational excitation have been examined in several reviews (see, for example, Bauer⁶⁸ and Zewail¹²⁶).

We are interested in bimolecular reactions of polyatomic molecules with a sufficiently high vibrational energy. The concept of the vibrational mode loses significance for such molecules and their reactivity depends primarily on the total vibrational excitation energy or, more precisely, on the distribution function with respect to the total vibrational energy.

Analysis of the activation characteristics of bimolecular reactions remains the first and so far the only systematic method for the kinetic determination of the specific rate constants for bimolecular reactions of the HES of polyatomic molecules.⁶⁹

The principal idea underlying the activation mechanism is illustrated by the following Scheme 1.

Scheme 1

Unimolecular reactions	Bimolecular reactions
$A \longrightarrow \text{products}$	$A + B \longrightarrow \text{products}$
$A + M \xrightleftharpoons[k_{-a}]{k_{+a}} A^* + M$	$A + M \xrightleftharpoons[k_{-a}]{k_{+a}} A^{**} + M$
$A^* \xrightarrow[k(E \geq E_m)]{k(E)} \text{products}$	$A^{**} + B \xrightarrow[k(E \geq E_{\text{bim}})]{k_b(E)} \text{products}$
$k_d = \frac{k(E)(k_{+a}/k_{-a})}{1 + (k(E)/k_{-a}M)}$	$k_{\text{bim}} = \frac{k_b(E)(k_{+a}/k_{-a})}{1 + (k_b(E)[B]/k_{-a}[M])}$
Limiting cases	
Equilibrium regime	
$[M] \longrightarrow \infty$	$\frac{k_b(E)}{k_{-a}} \xi_B \ll 1$
$k_{d,\infty} = \frac{k(E)k_{+a}}{k_{-a}}$	$k_{\text{bim},\infty} = \frac{k_b(E)k_{+a}}{k_{-a}}$
Regime limited by activation	
$[M] \longrightarrow 0$	$\frac{k_b(E)}{k_{-a}} \xi_B \gg 1$
$k_{d,0} \simeq k_{+a}[M]$	$k_{\text{bim},0} \simeq \frac{k_{+a}}{\xi_B}$

A^* and A^{**} are active molecules which have acquired in activating collisions an amount of energy greater than the barrier to the unimolecular (E_m) and bimolecular (E_{bim}) reactions respectively; ξ_B is the mole fraction of component B in the mixture.

The dependences of the observed bimolecular reaction rate constant on mixture composition can be conveniently referred to as transition curves by analogy with unimolecular reactions. We shall now formulate the relations which have been established on the basis of the interpretation of the fall-off curves for the rate constants for bimolecular reactions involving nitrogen oxides (Table 4).

1. The ratio $\bar{k}_b/k_{-a}$ is in the range 4–20. Here $\bar{k}_b$ is the rate constant for the bimolecular reaction averaged for the energies above the barrier E_{bim} and k_{-a} is the deactivation rate constant.

2. The constant k_b depends both on the store of vibrational energy and on the gas temperature. The translational barrier to the bimolecular reaction of the HES is $\sim 10\%$ of the overall barrier.

Table 4. Rate constants for bimolecular reactions (k_{bim}) and the effectiveness of collisions (β_c) for highly excited states of the NO_2^* and N_2O molecules.

Reaction	$\bar{k}_b/Z_{\text{gk}}^a$	T/K	E_b /kcal mol ⁻¹	$10^2\beta_c^b$
$\text{N}_2\text{O}^* + \text{NO}$	0.08	1680	41	0.4
$\text{N}_2\text{O}^* + \text{CO}$	0.06	1590	54	0.3
$\text{NO}_2^* + \text{NO}_2$	0.14	1670	39	0.3

Note. 1. The results for k_b and β_c were obtained on the basis of a theoretical description of the transition curves (Fig. 17). 2. The dependence of β_c on the excitation energy is fitted by the relation $\beta_c \simeq E^2$. 3. The dependence of k_b on the translational temperature T_g is fitted by the equation $k_b \simeq \exp(-E/RT)$, where E is the translational barrier to the reaction of the vibrationally excited molecule.

^a $\bar{k}_b$ is the average value in the region $E > E_b$ (the bimolecular reaction barrier) and Z_{gk} is the frequency of the gas-kinetic collisions. ^bThe value of β_c for the excitation energy in the vicinity of the barrier to the bimolecular reaction: $\beta_c \simeq \langle E \rangle^2$.

3. The observations for k_b have been interpreted on the basis of the collision-stochastic model, according to which during the period of the interaction of the reactants all the vibrational modes of the polyatomic molecules contribute to the reaction rate (we may note that this property is fully correlated with the multiple ‘chattering’ collisions mechanism).

4. The activation characteristics are observed only for reactions with a high barrier, *i.e.* their rates increase markedly at high temperatures.

The question arises why nonequilibrium effects involving depletion of the distribution function with respect to vibrational energy in the vicinity of the barrier are manifested precisely for reactions with fairly high barriers. This can be naturally attributed to the fact that, for reactions of polyatomic molecules with a sufficiently high level of excitation, the vibrational motion of the active molecules is nearly stochastic and the reactivity therefore increases as a consequence of the contribution of all the vibrational modes. Furthermore, the ratio k_b/k_{-a} , which determines the scale of the depletion of the distribution functions, increases with increase in temperature.

The distorting influence of bimolecular reactions of the HES of the NO_2 and SO_2 molecules on the form of the distribution function with respect to energy has been demonstrated.^{49, 56} In

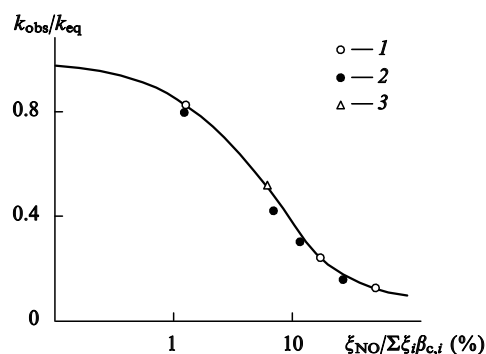


Figure 17. Transition curve for the rate constant for the exchange reaction $\text{N}_2\text{O} + \text{NO} \rightarrow \text{N}_2 + \text{NO}_2$: (1) 1% $\text{N}_2\text{O} + 2\%$ NO , 2.5% $\text{N}_2\text{O} + 97.5\%$ NO , Ar diluent; (2) recalculation of data in terms of inflammation limits; (3) 2.5% $\text{N}_2\text{O} + 25\%$ NO , CO_2 diluent. Data (1) and (3) were obtained in shock waves; ξ_i —mole fractions of the components; $\Sigma \xi_i \beta_{c,i}$ —the effectiveness of the partners $\beta_{c,i}$ in activating collisions averaged over the mixture; k_{obs} and k_{eq} —the observed rate constant for the bimolecular reaction and its equilibrium value respectively.

particular, this influence is fully correlated with the macroscopic manifestations of the state of nonequilibrium (Fig. 17).^{69–71}

An interesting development of the idea concerning the role of internal excitation on the reactivities of the partners in bimolecular reactions has been put forward.⁷⁴ The high effectiveness of the reactions under conditions where the reactants are ‘dissolved’ in a cluster which undergoes impact heating can be explained by the fact that the internal degrees of freedom of one or both reactants are excited by the cluster.

3. Generalising concepts for the bimolecular reactions of highly excited polyatomic molecules

It appears at first sight that the family of bimolecular reactions is so diverse that it is difficult to speak of any kind of generalising concepts. Fortunately such is not the case and we shall in fact attempt to illustrate this.

The statistical theory of bimolecular reactions rightfully occupies the central place in the list of such concepts. The possibilities of this theory have been best demonstrated in Troe’s review, which has been justifiably given the emotive title ‘The Colourful World of Bimolecular Reactions’.⁶²

Why is the rating of the statistical theory so high? There are two main reasons. Firstly, the wide occurrence of bimolecular reactions, proceeding via a stage involving the formation of a long-lived complex, has an effect; secondly the entire procedures of the RRKM theory are applicable to reactions of this kind, which creates the necessary preconditions for the development of an overall computational set up.

The second concept may be regarded as heuristic systematic treatment. Such systematic treatment is based on the subdivision of the activation barrier for the reaction into the contributions due to the vibrational and translational degrees of freedom and the significance of the coefficient of the utilisation of the vibrational energy in overcoming the barrier is assigned to the ratio of these contributions.^{2, 3, 129}

The collision-stochastic model may be considered as the third concept.⁷¹ Initially this concept was put forward to account for the high preexponential factors for the bimolecular exchange reaction rate constants (Table 5), after which experimental data confirming it were obtained also by laser activation of polyatomic molecules.

Table 5. The Arrhenius parameters for the rate constants for certain bimolecular exchange reactions of valence-saturated diatomic and triatomic molecules ($k = Ae^{-E/RT}$).

Reaction	$\lg A^a$	E^b	T/K
$N_2O + CO \longrightarrow CO_2 + N_2$	16.0	53	1400–3000
$N_2O + NO \longrightarrow NO_2 + N_2$	15.2	48	1360–1890
$NO_2 + NO_2 \longrightarrow NO_3 + NO$	14.8	34	1400–2300
$NO_2 + CO \longrightarrow CO_2 + NO$	14.4	33	1400–2300
$SO_2 + SO_2 \longrightarrow SO_3 + SO$	15.0	70	3000–4000
$CO_2 + C^{18}O \longrightarrow C^{18}O_2 + CO$	16.33	66.7	3000–4000
$CO_2 + ^{13}CO \longrightarrow ^{13}CO_2 + CO$	13.94	48.9	3000–4000

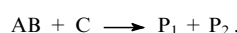
^a The dimensions of A are $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$. ^b The dimensions of E are kcal mol^{-1} .

If all the internal degrees of freedom contribute to the overcoming of the reaction barrier, then the equilibrium rate constant for bimolecular reactions k_{eq} is defined by the equation

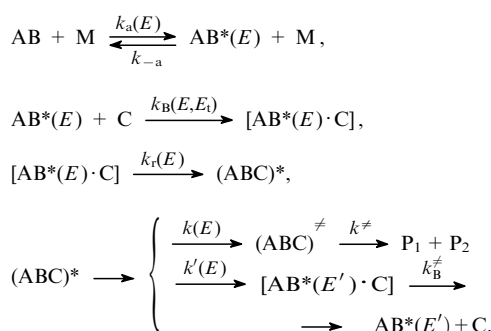
$$k_{\text{eq}} = A_{\text{eq}} \exp\left(-\frac{E_0}{RT}\right) = \int_{E_0}^{\infty} k_b(E_V, E_R T) f_0(E_V, E_{RT}) dE_V dE_{RT}. \quad (12)$$

Here A_{eq} is the pre-exponential factor, E_0 the activation energy for the equilibrium bimolecular reaction, $k_b(E_V, E_{RT})$ the rate constant for the bimolecular reaction as a function of the vibrational (E_V) and rotational-translational (E_{RT}) energy, and $f_0(E_V, E_{RT})$ the distribution function, proportional, in particular, to the density of the energy spectrum $\rho(E)$. The proportionality of k_{eq} to the total density of the spectrum $\rho(E)$ therefore follows from Eqn (12), which is in fact the reason for the high pre-exponential factors for the equilibrium bimolecular reaction rate constants.

If one is dealing with a detailed kinetic analysis of equilibrium rate constants for bimolecular reactions and hence for processes involving HES during the collision of the partners, then the simplest two-level mechanism must be supplemented by a more detailed consideration of processes involving excited molecules at the ‘inlet’ (initial reactions) and ‘outlet’ (reaction products). One of the versions of such consideration of the reaction



where AB and C are polyatomic molecules and P_1 and P_2 are the products, is presented in the following scheme:



Here $AB^*(E)$ is a molecule with an internal energy E , which is sufficient for it to react, $k_a(E)$ is the rate constant for activation in the energy range $E + dE$, $[AB^*(E) \cdot C]$ is the collision complex in which the distribution of energy is determined by the initial distribution of the internal energy of the fragments before collision and the relative motion of AB^* and C at the effective interaction potential, $k_B(E, E_t)$ is the rate constant for the ‘capture’ process indicated above, E_t is the energy of translational motion, $k_r(E)$ is the rate constant for the redistribution of energy in the collision complex, $(ABC)^*$ is the activated molecule in the traditional sense as understood in the RRKM theory, and $[AB^*(E') \cdot C]$ is the collision complex.

The flux of species through the configuration of the activated state is proportional to the partition function, so that the ratios of the vibrational-rotational partition functions of the collision complex (Q^*) and the activated molecule ($Q^{\#}$) must be compared in making a choice of the rate-limiting stage in the chain of transformations of the states involved in bimolecular reactions of active molecules. For the ratio of the vibrational-rotational partition functions, one may write

$$\frac{Q_{\text{vr}}^*}{Q_{\text{vr}}^{\#}} = \frac{Q_{\text{rot}}^*}{Q_{\text{rot}}^{\#}} \left(\frac{E_0}{RT}\right)^{(1/2)s_r^* + s_v^{\#}} \times \times \frac{E_0^{s_v^{\#} - s_v^*} F_E}{\Gamma[s_v^* + (1/2)s_r^* + 1]} \times \frac{\prod_i \hbar \nu_i^{\#}}{\prod_i \hbar \nu_i}, \quad (13)$$

where the * and # superscripts refer to the collision and activated complexes respectively, Q_{rot}^* and $Q_{\text{rot}}^{\#}$ are the rotational partition functions, s_v and s_r are the numbers of vibrational and rotational degrees of freedom, and F_E is a multiplier taking into account the energy dependence of the number of states of the collision complex with an energy greater than E_0 .

The ratio of partition functions defined by Eqn (13) depends on temperature. There exists a boundary temperature T_k at which

the ratio is close to unity. At $T > T_k$, the processes in the collision complex become rate-limiting and the bimolecular rate constant is determined by the redistribution of energy.

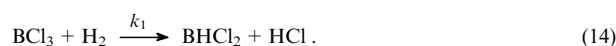
Turning now to specific examples, we may note that calculations of T_k by Eqn (13) yield 800–1400 K for the $N_2O^* + CO$ and $N_2O^* + NO$ reactions depending on the hypotheses concerning the parameters of the activated complex.⁷³

Thus the manifestation of nonequilibrium effects in bimolecular exchange reactions of polyatomic molecules depends greatly on the relation between the rate-limiting stages presented in Eqn (13) and is most probable for fairly high temperatures.

We may note, incidentally, that the deviations of the bimolecular rate constants from the equilibrium values are less pronounced than for the unimolecular decomposition reactions (Fig. 13). This is apparently one of the reasons why the non-equilibrium effects in bimolecular reactions were assumed to be relatively insignificant and did not receive sufficient attention.

One may postulate that the collision-stochastic model of bimolecular reactions is capable of yielding satisfactory results also for laser-stimulated reactions.

As an illustration, we shall consider the calculations for the reactions of BCl_3 molecules, excited by IR laser radiation, with H_2 molecules (energy ~ 1 J per pulse, duration of pulse 0.2 μs),¹³⁰ which confirms the principal postulates of the collision-stochastic model for bimolecular reactions. At a sufficiently high level of excitation, the chlorine atoms in the BCl_3 molecule are considered to have lost their permanent locations (as happens in the melting process in a solid) and they then move more independently and within the limits of the molecule may have significantly longer ‘free paths’. The ‘partly free’ chlorine atom subsequently reacts with the incoming H_2 molecule:

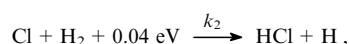


Several assumptions, taking into account the limitations to the mobility of the reactants within the limits of the initial molecules, are used in the calculations.

This model is a natural development of the ideas concerning the influence of the stochastic nature of the vibrations on the occurrence of bimolecular reactions and furthermore, as regards calculation, it represents a successful example of the application of relations employed in gas-phase and liquid-phase kinetics. In conformity with the model adopted, the reaction rate constant k_1 may be written in the form

$$k_1 = P_1 v_1 Q_1 \exp\left(-\frac{E_1}{T_1}\right),$$

where P_1 is the probability of the reaction



v_1 is the average relative velocity of BCl_3 and H_2 , Q_1 is the overall cross-section for the collision of H_2 and BCl_3 , E_1 is the activation energy for the reaction, and T_1 is the thermal energy of the H_2-BCl_3 ‘reacting mixture’. The reaction probability P_1 can be written in the form

$$P_1 = Z_{12} k_2 n_2 t,$$

where Z_{12} is the steric factor for the reaction of chlorine and hydrogen within the limits of the collision complex and k_2 is the gas-phase rate constant:

$$k_2 = v_2 Q_2 \exp\left(-\frac{2650K}{T_2}\right),$$

where v_2 is the relative velocity of BCl_3 and H_2 , Q_2 is the overall scattering cross-section for the H_2-Cl system, T_2 is the temperature at the centre of mass of the incoming hydrogen molecule and

chlorine in BCl_3 , and n_2 is the density of chlorine atoms in BCl_3 . The ‘contact time’ of the reactants is represented by the equation

$$t = \frac{1}{n_2 Q_2 v_2}.$$

The temperature of the chlorine atoms in this model is proportional to the kinetic energy of the atoms, equal to half the absorbed energy of the laser pulse (the second half represents the potential energy):

$$T_{Cl} = \frac{\hbar c n_v \bar{\nu}}{2 n_a (3/2) k_B} + T,$$

where n_v is the number of quanta of the laser radiation absorbed by the molecule, $\bar{\nu}$ the energy of the radiation quantum in cm^{-1} , n_a the number of atoms in the ‘hot molecule’, k_B the Boltzmann constant, and $(3/2)k_B$ the heat capacity of the translational degrees of freedom.

In the example of the heating of BCl_3 by the radiation from a CO_2 laser ($\nu = 950 \text{ cm}^{-1}$, $n_v = 10$, $n_a = 4$) considered by Kueba and Wolfrum,¹²⁸ $T_{Cl} \approx 1140 \text{ K} + T_1$ was obtained. The temperature at the centre of mass of the interacting H_2-Cl system is defined by the equation

$$T_{H_2-Cl} \approx T_{H_2} \left(1 + \frac{T_{Cl}}{T_{H_2}} \frac{M_{H_2}}{M_{Cl}}\right),$$

where T_{Cl} and M_{Cl} are respectively the temperature and the atomic weight of chlorine, $T_{H_2} = 300 \text{ K}$, and M_{H_2} is the molecular mass of hydrogen. T_{H_2-Cl} is found to be relatively low ($\sim 380 \text{ K}$) for the parameters quoted above.

Calculations performed with the aid of the above relations for the collision-stochastic model agree well with experimental data for the laser stimulation of the BCl_3-H_2 reaction.

In conclusion we shall note the most significant characteristic features of the activation mechanism of bimolecular reactions.

1. The vibrational energy of a polyatomic molecule is particularly effective in the bimolecular interaction of the partners when the reaction barrier is higher than the threshold of the transition to stochastic motion.

2. The stochastic nature of the vibrational motion explains the phenomenon of the so called multiplicity of collisions in the interaction of partners (the concept of a differentiated reaction coordinate then loses its significance; all these features together with the effect of the mixing of the modes are responsible for the high pre-exponential factors for the equilibrium rate constants [see Teitelbaum⁷³ and Table 5]).

3. The existence of the ‘translational barrier’ for bimolecular HES reactions is in essence equivalent to the introduction of the temperature at the centre of mass of the ‘hot’ molecule and the ‘cold’ partner.⁷¹

The above comparison indicates the conditions under which the traditional versions of the transition state method fail to work and should be replaced by the collision-stochastic model.

XI. Conclusion

The ‘hot’ band absorption spectroscopy of molecules makes it possible to investigate the influence of the form of the energy distribution function and of the dynamic parameters of the molecules on their absorption spectra, which constitutes the basis for the observation of highly excited molecules. The data on the properties of the distribution function then obtained are used in the analysis of kinetic processes with participation of HES on the basis of the solution of the fundamental microkinetic equation.

The emission technique in the visible, UV and IR regions of the spectrum, both in the traditional version and especially with Fourier transformation by virtue of the high sensitivity and high

time resolution, is very promising for the probing of HES distributions in reacting systems with thermal and laser pumping. The linkage between the optically active emitting electronic states and the highly excited states of the ground electronic term provides an instrument for the detection of these states and the energy distributions within the limits of both terms by virtue of reverse electronic relaxation.

The possibility of calibrating the 'hot' band absorption and emission spectra of polyatomic molecules constitutes one of the most important preconditions for the successful application of these methods in the study of nonequilibrium HES distributions.

Measurement of the kinetics of the transformation of HES distributions on thermal or laser pulse excitation is most productive in the determination of the HES energy exchange parameters in collisions.

The most realistic description of experimental data on the HES energy exchange kinetics in collisions is based on the superposition of strong and weak collisions.

In order to create an integral picture of the energy exchange and reactions of HES and also for the development of generalising concepts, it is necessary to carry out a joint analysis of the information obtained on the basis of both direct spectroscopic methods and indirect kinetic methods.

In conclusion, we shall make several predictive comments. Firstly, the ratio of computational and experimental studies will steadily change in favour of the former; the contribution of trajectory calculations will increase greatly. Secondly, the most promising way of developing the theory of processes with participation of HES involves the combination of trajectory calculations and simple basic models. Thirdly, DF calculations will be closely related to the spectra of the reacting components and calculations of this kind will become a standard procedure for investigators in the field of molecular and chemical kinetics.

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^a — *Russ. J. Chem. Phys. (Engl. Transl.)*

^b — *Quantum Electron. (Engl. Transl.)*

^c — *Russ. Phys. JETP (Engl. Transl.)*

^d — *Theor. Exp. Chem. (Engl. Transl.)*

^e — *Dokl. Chem. (Engl. Transl.)*

^f — *Kinet. Catal. (Engl. Transl.)*

Electrochemical reactions of organosilicon compounds

V V Jouikov

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Abstract. Data on the processes of electrochemical reduction and oxidation of organosilicon compounds of various classes as well as on the interaction of these compounds with electrically generated reagents are generalised and surveyed systematically. The electrochemical reactivity of organic derivatives of silicon is considered taking into account their structures and reaction conditions. The bibliography includes 245 references.

I. Introduction

Electrochemical procedures are widely used for the synthesis of various organic and organoelement compounds including organic derivatives of silicon, the chemistry of which has developed especially intensely in recent years. Up to now, vast experimental material has been accumulated in this field. On the one hand, numerous highly selective preparative procedures for the synthesis of target products or intermediates of the functionalisation of organosilicon compounds have been developed. On the other hand, in the studies of redox reactions involving these compounds, a clear-cut relationship between various intramolecular interactions and electrochemical reactivity has been elucidated. Thus, the electrochemistry of organosilicon compounds, apart from its purely preparative aspect, is necessarily concerned with the problems of physical organic chemistry, *i.e.* the structures of the frontier orbitals, transfer of electronic effects in the molecules and their influence on reactivity.

The purpose of this review is to consider systematically the known processes, classifying them according to the type of reaction and to follow, where possible, the roles of various factors determining the reactivity of organosilicon compounds in electrochemical transformations.

II. Electroreduction of chlorosilanes

Chlorosilanes are among the first organic derivatives of silicon synthesised. At present, they are the most frequently encountered and most readily accessible organosilicon compounds. Apparently, it is for this reason that chlorosilanes were first to attract the attention of electrochemists. Chlorosilanes themselves are difficult to reduce electrochemically, and the cathodic processes involving them are associated most frequently with the initial electrogeneration of a carbanion (or another nucleophile), which then replaces a Cl atom in the chlorosilane molecule. Most of the cathodic reactions involving chlorosilanes are versions of this process. Anodic processes involving organosilicon compounds are more diverse (regarding the types of compounds and reactions), although the number of publications dealing with reduction is much greater than that on oxidation.^{1–13}

The first studies on the electrochemistry of chlorosilanes (R_nSiCl_{4-n} , where $R = Me, Et, Vin, Ph$) were published more than twenty years ago;^{14–16} however, they were only indirectly associated with the problem under consideration, because they described electroreduction of the protons of the hydrogen chloride arising *via* hydrolysis of chlorosilanes.^{14, 17–20} Nevertheless, these studies have resulted in the development of two efficient methods: a method for electrochemical dehydration of dimethylformamide (DMF)²¹ and a procedure for determining the quantity of water in this solvent.²² Both methods are based on fast hydrolysis of chlorosilanes.

Later, various researchers have obtained electrochemical characteristics for the reduction of chlorosilanes (Table 1); these characteristics were markedly dissimilar even for the same compounds. Since the reduction of chlorosilanes is irreversible and they are highly electrophilic and extremely susceptible to hydrolysis, the effective reduction potentials of these compounds are influenced by many factors (material of the electrode, solvent, supporting electrolyte and, obviously, nucleophilic impurities). Therefore, the fairly contradictory data presented in Table 1 can be rather regarded as an illustration of the confusion reigning in this field. It can be only noted that the nature of the halogen (all other factors being equal), apparently, exerts no significant influence on the reduction potentials.^{23, 24} The nature of the organic substituent at the Si atom is more important. Chlorotrimethylsilane **1** accepts an electron at a more negative potential than chlorotriphenylsilane **2**,²⁵ although the discussion about the

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Table 1. Characteristics of electroreduction of chlorosilanes (the first wave for polychlorosilanes).

Chlorosilane	E/ V (vs SCE)		Conditions	Ref.
	$-E_{1/2}$ / V	$-E_p$ / V		
Me ₃ SiCl (1)	2.2 ^a	0.1	DME/Bu ₄ NClO ₄ /Pt	36
			DME/Bu ₄ NClO ₄ /Pt	37
		3.3 ^b		29
		1.11 ^c	PhOMe/Bu ₄ NClO ₄	18
Ph ₃ SiCl (2)	3.1 ^a 2.39		DMF/Et ₄ NOTs	28
			DME/Bu ₄ NClO ₄ /Hg	22, 39
			THF/Bu ₄ NClO ₄ /Hg	23, 40
		0.2	DME/Bu ₄ NClO ₄ /Pt	36
MePh ₂ SiCl (3)	1.2		DME/Bu ₄ NClO ₄	37
		2.4 ^b		29
		2.55	AN/Bu ₄ NPPH ₄ /Pt	27
		2.65	AN/Bu ₄ NClO ₄ /GC	38
Ph ₃ SiBr	2.37		DME/Bu ₄ NClO ₄ /Hg	40
Ph ₃ SiF	2.59 ^d		DME/Bu ₄ NClO ₄ /Hg	40, 24
Me ₂ SiCl ₂ (4)		2.28 ^e	DME/Bu ₄ NBF ₄ /Hg	41
		> 2.5		42
PhMeSiCl ₂ (5)		> 1.8		42
Ph ₂ SiCl ₂ (6)	1.9 ^a	2.5	AN/Bu ₄ NClO ₄ /GC	38
			DME/Bu ₄ NClO ₄ /Hg	39, 43
		> 1.5		42
Mes ₂ SiCl ₂ (7)	2.8 ^f		DME/ME	44
SiHCl ₃	1.7–1.75 ^b		AN/Et ₄ NCl/graphite	45
		1.9 ^g	THF/Pt	46
SiCl ₄	1.66–1.70 ^b		AN/Et ₄ NCl/graphite	45
		2.2 ^b	THF/Pt	46

Note. SCE is saturated calomel electrode, DME is dimethoxyethane, DMF is *N,N*-dimethylformamide, THF is tetrahydrofuran, AN is acetonitrile, GC is glassy carbon, Mes is mesityl, ME is dropping-mercury electrode.

^a vs 0.001 M Ag/AgClO₄; ^b vs. Ag/AgCl; ^c vs. Ag/AgNO₃; ^d vs. Ag/AgI (recalculated for SCE); ^e apparently, the E_p value is presented; ^f vs. Ag/Ag⁺ ($E = E_{\text{SCE}} + 0.6$ V); ^g reduction of the Si–H bond.

potential for the cathodic reduction of the silane **1** has not yet been completed.^{23, 26–37}

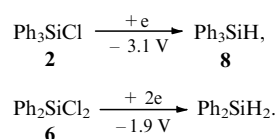
The reduction potentials of most of the studied chlorosilanes, determined by various authors, have relatively large negative values (Table 1). Evidently, this is due to an activation mechanism of the electron transfer, which is accompanied by the simultaneous rupture of the Si–Cl bond. Jammegg *et al.*³⁶ claim that the peaks they detected at -0.1 and -0.2 V (vs SCE) refer to the products of reduction of this bond, although no products with the Si–Si bond were detected after the electrolysis of the chlorosilane **1** at $E \approx -1$ V. It follows from the experimental procedure described in this study that the researchers aimed at minimising the content of the residual water and HCl but ignored the presence of dissolved oxygen, which produces reduction peaks in this range of potential. Therefore, the signals at -0.1 and -0.2 V are most likely associated with the reduction of oxygen.³⁶

An important role in the electrochemical reduction of chlorosilanes belongs to the solvent^{23, 24, 32–34} and to the supporting electrolyte used,³⁵ because nucleophilic solvents can be coordinated by chlorosilanes, and, consequently, the silicon atoms acquire a planar configuration favourable for nucleophilic reactions.

The reduction of 6,6-dichloro(or fluoro)-6*H*-dibenzo-[*c,e*][1,2]oxasilanes in the DME/Bu₄NI system occurs as a single-electron reduction of the phenanthrene type ring ($E_{1/2} = -1.96$ and -0.96 V vs Hg pool for fluoro- and chloro-derivatives, respectively) and the subsequent two-electron transfer accompa-

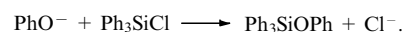
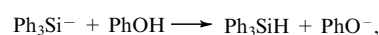
nied by the abstraction of a halogen ($E_{1/2} = -2.31$ and -1.41 V vs Hg pool).⁴⁷

The products obtained by electroreduction of chloro(phenyl)silanes in DME have been identified as phenylsilanes based on a comparison of their UV spectra with the spectra of individual compounds.³⁹



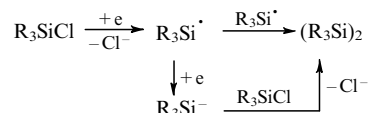
(The E values are given with respect to 0.001 M Ag/AgClO₄.)

It has been believed that DME or the Bu₄N⁺ cation serves as the source of the hydrogen atoms needed for the formation of silanes. According to more recent studies,^{37, 48–52} reduction of chloro(phenyl)silanes under similar conditions yields mostly di- and tetra-silanes. Nevertheless, the results of the electrolysis of chlorotriphenylsilane **2** in the presence of phenol serving as a donor of protons²³ attest to the formation of the Ph₃Si[−] anion, because this reduction affords hydride **8** rather than the dimer. The fact that 1 F of electricity is consumed for the reduction of 1 mole of the chlorosilane **2** indicates that the electrode process includes the reaction between the nucleophile PhO[−] and the initial chlorosilane molecule.



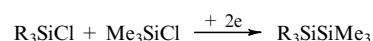
When chlorotrimethylsilane **1** was reduced in MeCN using Bu₄NClO₄ as the supporting electrolyte, hexamethyldisiloxane was obtained, whereas in the presence of Bu₄NCl, the process gave hexamethyldisilane **9**.²⁵ Electroreduction of chlorosilane **1** in DME with a platinum or lead cathode and mercury anode^{48, 53} under non-controlled conditions (output voltage 80 V, current density 1–6 mA cm^{−2}) for 4–10 days gives rise to disilane **9** in a current yield of 100%.³⁷ The researchers³⁷ mentioned that the disilane **9** was also produced at the anode; however, since the electrolysis was carried out in an undivided cell, they were, most likely, mistaken.

It is assumed that the electrosynthesis of disilanes from chlorosilanes R₃SiCl in aprotic solvents follows two competing pathways.^{23, 24, 40} The first pathway includes nucleophilic interaction of the R₃Si[−] anion (resulting from the two-electron reduction of chlorosilane) with the initial chlorosilane, while the second pathway consists in the radical dimerisation of the products of its single-electron reduction (R₃Si[•] radicals).



Electroreduction of a great number of monochlorosilanes occurs with the consumption of 1 F mol^{−1} of electricity and yields symmetrical disilanes (Table 2).

Table 3 presents the results of preparative electroreduction of mixtures of chlorosilanes giving asymmetrical disilanes with various substituents at the silicon atoms. Electrolysis of a 1 : 1 mixture of triarylchlorosilane and chlorotrimethylsilane **1** yields an asymmetrical disilane as the only product; hence, this is a convenient method for the synthesis of these compounds.



R = Ph, *p*-FC₆H₄, *p*-MeC₆H₄.

The above proves that triarylchlorosilane rather than chlorotrimethylsilane is the first to be reduced.³⁷ The reduction of

Table 2. Cathodic synthesis of symmetrical disilanes by electroreduction of chlorosilanes $R^1R^2R^3SiHal$.

Chlorosilane	Product	Conditions of electrolysis ^a	Yield (%)	Ref.
Me_3SiCl (1)	$(Me_3Si)_2$	Mg anode and cathode, THF/ $LiClO_4$	100 ^b	25
		THF : HMPT (8 : 2)/ $LiCl$, $AlCl_3$, Bu_4NBr , $Al(Mg)$ anode, SS cathode	93	29
		Mg anode and cathode, THF/ $LiClO_4$	74–78	41
		Silicon carbide anode, THF/HMPT	82	51
		Hydrogen anode, THF/HMPT	65 ^b	36
			73 ^b	36
Me_3SiBr	$(Me_3Si)_2$		20	25
$Me_2PhSiCl$ (10)	$(Me_2PhSi)_2$	THF : HMPT (8 : 2)/ $LiCl$, $AlCl_3$, Bu_4NBr , $Al(Mg)$ anode, SS cathode	80–83	41
		Hg anode, Pt cathode in DME	84 (37 ^b)	54
		Mg anode and cathode, polarisation by alternating current in THF/ $LiClO_4$	92 (69.5 ^c)	51
		The same in THF/ $LiBF_4$	2.3 (10 ^c)	51
		The same in THF/ Bu_4NClO_4	75.1 (49.6 ^c)	51
		The same in THF/ Bu_4NBF_4	11.7 (2.0 ^c)	51
$MePh_2SiCl$ (3)	$(MePh_2Si)_2$	THF : HMPT (8 : 2)/ $LiCl$, $AlCl_3$, Bu_4NBr , $Al(Mg)$ anode, SS cathode	60–68	49
		Hg anode, Pt cathode in DME	89 (57 ^b)	54
		Al anode, Pt cathode in DME	47 (40 ^b)	54
		Ag anode, Pt cathode in DME	85 (62 ^b)	54
		Mg anode and cathode, THF/ $LiClO_4$	77	51
		Cu anode and cathode, DME/ Bu_4NClO_4	83	55
Ph_3SiCl (2)	$(Ph_3Si)_2$	Cu anode and cathode, DME/ Bu_4NBPPh_4	84	35
		Hg, Cd anode, Pt(Hg, Pb, Ti, Fe) cathode, DME/ Bu_4NClO_4	100 ^b	37
		THF : HMPT (8 : 2)/ $LiCl$, $AlCl_3$, Bu_4NBr , $Al(Mg)$ anode, SS cathode	70–71	49
		Mg anode and cathode, THF/ $LiClO_4$	85	51
		The same	78	56
		Hg, Cd anode, Pt(Hg, Pb, Ti, Fe) cathode, DME/ Bu_4NClO_4	82 ^b	37
$PhCH_2Me_2SiCl$	$(PhCH_2Me_2Si)_2$	The same	50 ^b	37
$(p-FC_6H_4)_3SiCl$	$[(p-FC_6H_4)_3Si]_2$	The same	0.3	37
$(p-FC_6H_4)_2MeSiCl$	$[(p-FC_6H_4)_2MeSi]_2$	The same		37
$Ph_3SiSiPh_2Cl$	$(Ph_3SiPh_2Si)_2$	The same		37
$Me_3SiSiPhMeCl$	$(Me_3SiPhMeSi)_2$	Cu anode and cathode, DME/ Bu_4NClO_4	90	55

^a HMPT is hexamethylphosphoric triamide; SS is stainless steel; ^b current yield; ^c the values obtained under the same conditions but using DME instead of THF are given in parentheses.

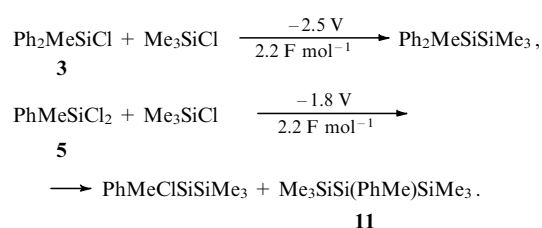
Table 3. Cathodic synthesis of asymmetrical disilanes by joint electroreduction of arylchlorosilanes and chlorotrimethylsilane **1**.

Chlorosilane	Product	Conditions of electrolysis	Yield (%)	Ref.
$Me_2PhSiCl$ (10)	$Me_2PhSiSiMe_3$	Hg anode, Pt cathode in DME/ Bu_4NClO_4	72 (22 ^a)	54
		$Al(Mg)$ anode, SS cathode, THF/TDA ^b (HMPT)	80–83	49
$MePh_2SiCl$ (3)	$MePh_2SiSiMe_3$	Hg anode, Pt cathode in DME/ Bu_4NClO_4	77	55
		Ag anode, Pt cathode in DME/ Bu_4NClO_4	78 (65 ^a)	54
		Hg anode, Pt cathode in DME/ Bu_4NClO_4	94 (30 ^a)	54
		$Al(Mg)$ anode, SS cathode, THF/TDA ^b (HMPT)	90 ^b	41
		Hg anode, Pt cathode in DME/ Bu_4NClO_4	78 (30 ^a)	54
Ph_3SiCl (2)	$Ph_3SiSiMe_3$	Hg, Cd anode, Pt(Hg, Pb, Ti, Fe) cathode, DME/ Bu_4NClO_4	6.5 (100 ^a)	37
		$Al(Mg)$ anode, SS cathode, THF/TDA ^b (HMPT)	74–77	49
		Hg, Cd anode, Pt(Hg, Pb, Ti, Fe) cathode, DME/ Bu_4NClO_4	46 ^a	37
$(p-FC_6H_4)_3SiCl$	$(p-FC_6H_4)_3SiSiMe_3$	Hg, Cd anode, Pt(Hg, Pb, Ti, Fe) cathode, DME/ Bu_4NClO_4	61 ^a	37
$(p-MeC_6H_4)_3SiCl$	$(p-MeC_6H_4)_3SiSiMe_3$	Hg, Cd anode, Pt(Hg, Pb, Ti, Fe) cathode, DME/ Bu_4NClO_4	46	37
$(p-F_3CC_6H_4)_3SiCl$	$(p-F_3CC_6H_4)_3SiSiMe_3$	Hg, Cd anode, Pt(Hg, Pb, Ti, Fe) cathode, DME/ Bu_4NClO_4	74 ^d	55
$Me_3SiSiPhMeCl$	$Me_3Si(PhMe)SiSiMe_3$	Cu anode, Pt(Cu) cathode in DME/ Bu_4NClO_4		55

^a Current yield; ^b TDA is tris(3,6-dioxaheptyl)amine; ^c using Me_2Bu^tSiCl instead of Me_3SiCl ; ^d 4% of a symmetrical tetrasilane was also obtained.

chloro(methyl)diphenylsilane **3** (to give disilane in 90% yield) and dichloro(methyl)phenylsilane **5** occurs according to a similar scheme.^{57†} In the latter case, trisilane **11** is formed in 25% yield, together with the monosilylation product formed in 75% yield.

† From this point on, the amounts of electricity (Q) consumed in the electrolysis per mole of the substance were taken from the original publication; in those cases where the original source contains no coulometry data, the numbers of electrons per molecule (n) calculated according to the stoichiometry of the process are presented in the schemes.

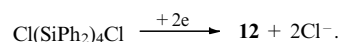
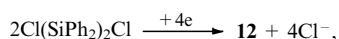
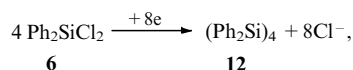


Since the chlorosilane **1** is more difficult to reduce than most other chlorosilanes,^{27–29} while the rate of nucleophilic substitution in **1** is markedly higher than the rate of the S_N2 reaction

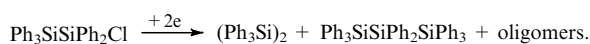
involving the second chlorosilane, asymmetrical chlorosilanes are formed predominantly. It is noteworthy that Bordeau *et al.*⁴⁹ obtained only an asymmetrical product in the reduction of a mixture of two chlorosilanes, whereas other researchers^{37, 58} have detected some quantity of a symmetrical disilane (derived from the chlorosilane, the reduction potential of which was less negative) in the reaction products; finally, Shono⁵⁶ has reported that equal amounts of symmetrical and cross-disilanes are formed.

The reduction of chlorosilanes R_3SiCl and $R_2R'SiCl$ yields symmetrical dimeric derivatives $(R_3Si)_2$ and $(R_2R'Si)_2$ as the major products (see Table 3). In the case of the chlorosilanes **1** and **2**, these dimers are obtained in nearly quantitative yields,³⁷ while in the case of bromotrimethylsilane, the yield of the dimer is 20%, and iodotrimethylsilane gives no dimer at all.^{25, 43} It should be noted that symmetrical and asymmetrical disilanes are produced in good yields in the electrochemical reactions of appropriate chloro-derivatives even in those cases where the corresponding chemical reactions with metals give no results.

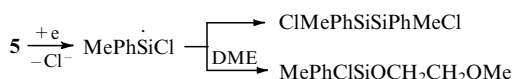
The main products resulting from the reduction of dichlorosilanes are the corresponding polysilanes.^{37, 43, 48} Thus the electroreduction of dichlorodiphenylsilanes under conditions similar to those described in Ref. 37 yields insoluble octaphenylcyclotrasilane **12** and some quantity of polymeric products.⁴⁸



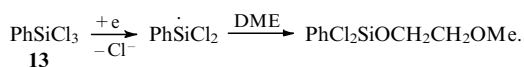
Reduction of chloropentaphenyldisilane has led to a mixture of products.⁴⁸



The reactions of chloro(methyl)phenylsilanes follow a more complex pathway. For example, in the case of dichloro(methyl)phenylsilane **5**, apart from the dimer, a product resulting from reaction with DME used as the solvent was obtained.

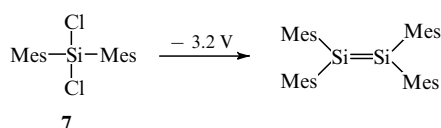


Data on the cathodic reduction of trichlorosilanes are contradictory. It has been reported⁴⁸ that electrolysis of PhSiCl_3 **13** also affords a product formed in reaction with the solvent.



The fact that no polymeric compounds with Si–Si bonds were detected among the reaction products was explained⁴⁸ by steric reasons. Conversely, the electrolysis of MeSiCl_3 results in the formation of the polymer $(\text{MeSiCl}_{0.22})_n$ unstable in air, while the electrolysis of SiCl_4 gives rise to the polymer $(\text{SiCl}_{0.77})_n$.^{28, 59}

A rare case where tetramesityldisilene is formed in the reduction of dichlorodimesitylsilane has been described.⁴⁴ This is the only example of electrosynthesis of a compound incorporating a Si = Si double bond.

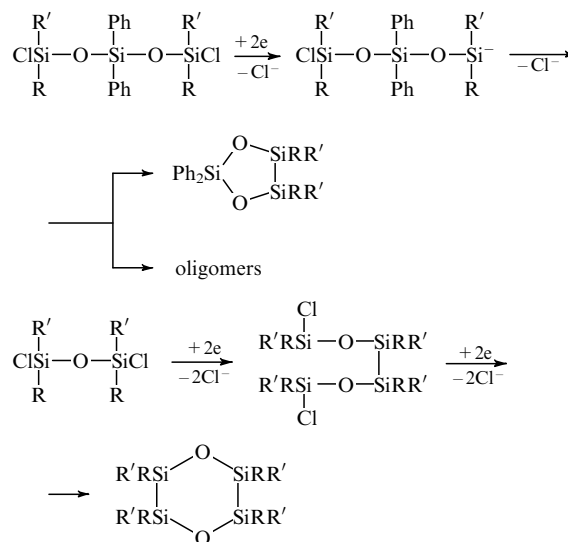


7

The reduction of dichlorodimesitylsilane **7** was carried out in the potentiostatic regime at $-3.2 \text{ V vs Ag/Ag}^+$ in DME/ $\text{Bu}_4\text{N}-\text{ClO}_4$ using an Hg cathode and an Ag anode with separated

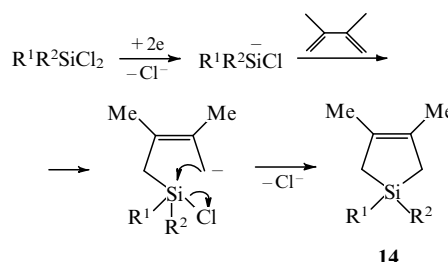
cathode and anode chambers. The yield of tetramesityldisilene of the 'pure for analysis' grade amounted to 20%.

Electroreduction of terminal dichlorosiloxanes affords cyclic compounds containing Si–O and Si–Si bonds.^{30, 60, 61} The five-membered cyclic product is formed in one step, while the six-membered product is formed *via* a linear dimeric dichlorodisiloxane, which can be isolated from the reaction mixture.



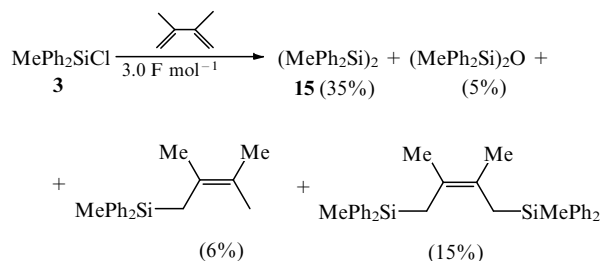
R, R' = Me, Vin, Et.

When silyl intermediates generated at the cathode react with 2,3-dimethylbutadiene, 1,1-disubstituted 3,4-dimethyl-1-silacyclopent-3-enes **14** are produced together with linear polysilanes.³⁸



The results of cathodic electrosynthesis of substituted silacyclopentenes **14** under various conditions are presented in Table 4.

Electrosynthesis involving the monochlorosilane **3** and carried out in DME with tetrabutylammonium perchlorate as the supporting electrolyte yields symmetrical disilane **15**, some quantity of disiloxane and products resulting from the addition to the diene, namely, 1-(methyldiphenylsilyl)-2,3-dimethylbut-2-ene and 1,4-bis(methyldiphenylsilyl)-2,3-dimethylbut-2-ene.



Trimethyl(phenylethynyl)silane **16** is formed in the electroreduction of halotrimethylsilanes Me_3SiHal (Hal = I, Cl, F)^{31, 62–64} in the presence of phenylacetylene **17**. Using the method of latent limiting currents, the stoichiometry of the interaction of the latter with electrically generated silyl anions was found to be 1 : 1. This corresponds to the protonation of the silyl anion by phenylacetylene to give the $\text{PhC}\equiv\text{C}^-$ carbanion, which substitutes

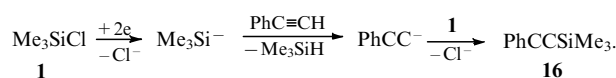
Table 4. Electroreduction of dichlorosilanes in the presence of 2,3-dimethylbutadiene.

Chlorosilane	Chlorosilane/ /diene (mmol)	Solvent/electrolyte	$Q/F \text{ mol}^{-1}$	Yields of the sila- cyclopentenes 14 (%) ^a	Yield of the polymer (%) ^a
MePhSiCl ₂	5.8/16.1	DME/Bu ₄ NClO ₄	1.7	10	9
Ph ₂ SiCl ₂	4.9/14.7	DME/Bu ₄ NClO ₄	2.4	27	41
	5.0/14.9	DME/Bu ₄ NBPh ₄	3.5	23	38
	5.0/15.8	THF/Bu ₄ NClO ₄	3.0	23	42
	3.1/9.9	THF/Bu ₄ NBPh ₄	2.8	28	44
(<i>o</i> -Tol) ₂ SiCl ₂	5.2/15.9	DME/Bu ₄ NBPh ₄	7.0	10	4
(<i>p</i> -Tol) ₂ SiCl ₂	4.8/16.0	DME/Bu ₄ NClO ₄	1.6	4	5 ^b

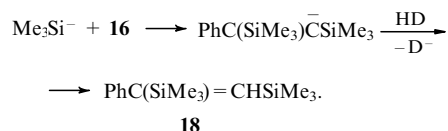
Note. Conditions of the electrolysis: Pt cathode, Cu anode, undivided cell, galvanostatic regime, current density 3.3 mA cm⁻².

^a Chromatographic yields are presented; ^b the yield of octa-*p*-tolylcyclotetrasiloxane is presented.

nucleophilically the chlorine in a molecule of the initial chlorosilane **1**.

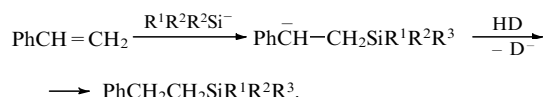


The compound **16** can be once again silylated. In this case, the process is accompanied by a decrease in the multiplicity of the bond and affords a nucleophilic addition product, 1,2-bis(trimethylsilyl)-1-phenylethene **18**.

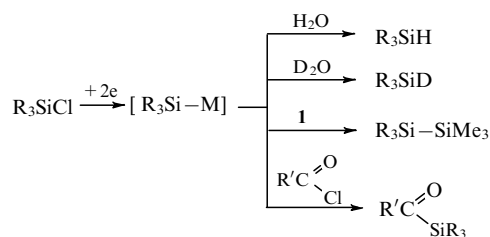


It is of interest that when this process is conducted at a **1**:**17** ratio of 4:1 by passing 5 F mol⁻¹ of electricity in a flow-type electrolyser consisting of two coupled cells³¹ (an ECE cell), in which the R¹R²R³Si⁻ anions electrically generated at the cathode of the first cell are partially oxidised in the second cell to give R¹R²R³Si[•] radicals, disilylated product **18** is obtained in a yield of up to 75%.

Under similar conditions, styrene yields only products of addition at the double bond.⁶³

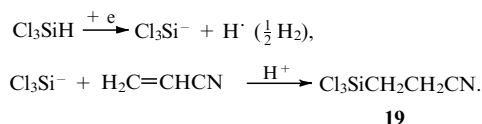


Silyl anions resulting from the reductive cleavage of the Si–Cl bonds in chlorosilanes can be ‘stabilised’ as organometallic intermediates *via* the formation of a Si–M bond (M is the metal that forms the soluble anode). The nature of these intermediates is not completely clear, but they can be kept in solution for several days and used in reactions with electrophilic reagents.^{27, 65, 66}



Cyclohexylsilyl derivatives have been prepared by electroreduction of a number of chlorosilanes in the presence of cyclohexene.^{63, 67–70} Since cyclohexene is not prone to enter into nucleophilic substitution, this reaction was suggested to occur by a radical mechanism.

It has been reported⁴⁵ that the intermediates formed in the electroreduction of tetrachlorosilane do not react with acrylonitrile, although the same researchers have described⁴⁶ a reaction of silyl anions electrically generated by the reduction of the Si–H bond in trichlorosilane (at $E = -1.6 \text{ V vs Ag/AgCl}$) with acrylonitrile to give trichloro(β-cyanoethyl)silane **19**.⁴⁶

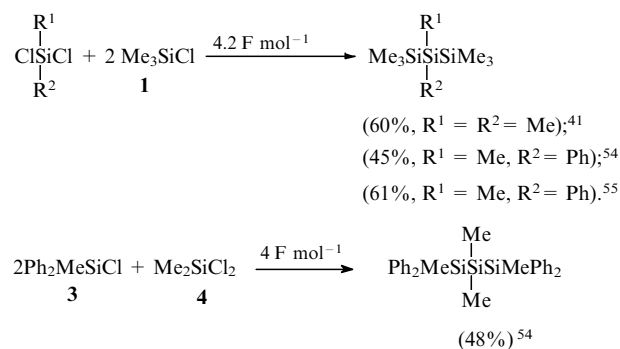


The compound **19** can also be obtained from trichlorosilane and acrylonitrile by a purely chemical procedure, namely, radical hydrosilylation. Therefore, it is quite probable that either the signal of reduction of SiCl₄ (Table 1) does not refer to the reduction of a Si–Cl bond or the rate of interaction of the electrically generated Cl₃Si⁻ anions with the highly electrophilic SiCl₄ molecule is much higher than the rate of the addition at the double bond.

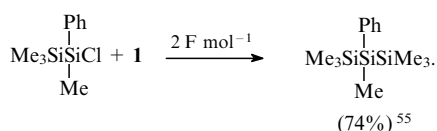
III. Cathodic syntheses of tri- and poly-silanes

Polysilanes (–Si–)_{*n*} containing more than two silicon atoms in the chain can be obtained by coupling of two chlorosilanes during their joint reduction, which leads to the formation of one or two Si–Si bonds. Chloro-derivatives of di-, tri- and poly-silanes are used as the initial monomers, depending on the required length of the chain of silicon atoms.

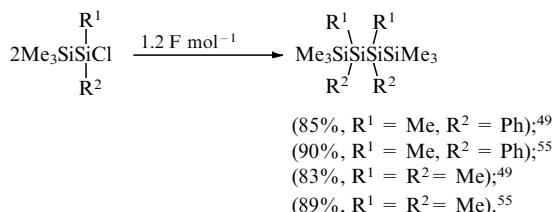
Electrosynthesis of trisilanes is carried out by the following schemes.



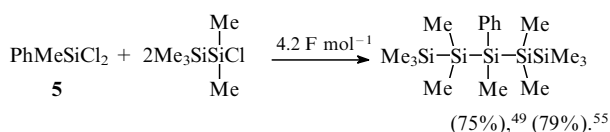
Trisilanes are also formed in the reductive coupling of chlorodisilanes and the chlorosilane **1**, for example:



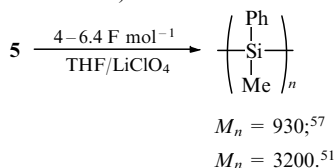
Electrosynthesis of tetrasilanes is accomplished by coupling of disilanes.



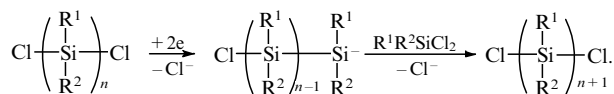
Electrosynthesis of pentasilanes is accomplished by coupling of dichlorosilanes and chlorosilanes.



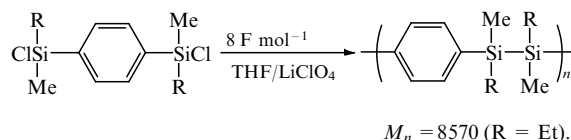
Electroreduction of a number of chlorosilanes [for example, dichloro(methyl)phenylsilane **5** and 1,4-bis(dialkylchlorosilyl)benzenes^{51,56}] at Mg electrodes in an undivided cell affords polysilanes in 5%–26% yields. It has been noted that treatment of the reaction mixture with ultrasound with a frequency of 47 kHz leads to a substantial increase in the yield of polysilanes (to 33%–45%).⁵¹



It has been assumed that the formation of polysilanes in the electroreduction of dichlorosilanes involves an ionic mechanism for the chain lengthening consisting of a number of electroreduction– S_N2 successive steps.⁵⁶ The initial molecule characterised by a more negative reduction potential undergoes the nucleophilic attack.

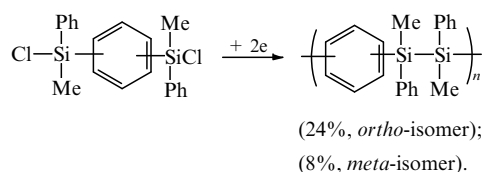


The reduction of 1,4-bis[chloro(methyl)phenylsilyl]benzene in THF/LiClO₄ with polarisation by alternating current and with ultrasonic treatment of the reaction mixture leads to a polymer consisting of the (–C₆H₄–SiSi–) units.

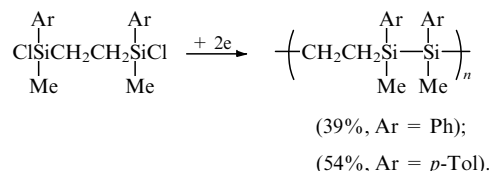


When the amount of the electricity passed is increased from 8 to 12 F mol^{–1}, the molecular mass of the polymer M_n (at $\text{R} = \text{Et}$) increases to 9960.⁵⁶

The reduction of *ortho*- and *meta*-substituted bis[chloro(methyl)phenyl]benzene at a Pt cathode (Cu anode, DME/Bu₄NClO₄ or Bu₄NBPh₄) in the galvanostatic regime also yields disilanylene polymers.⁷¹



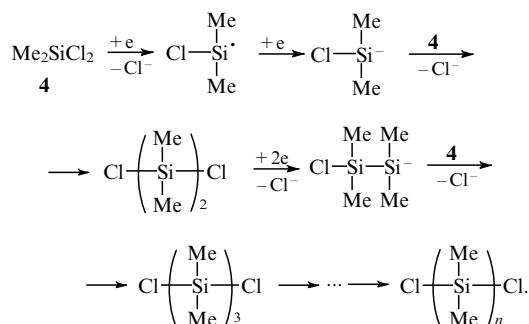
Polymeric products with high molecular masses consisting of the (–CH₂CH₂–SiSi–) fragments have been prepared by electroreduction of 1,2-bis[chloro(methyl)phenylsilyl]ethane and 1,2-bis[chloro(methyl)(*p*-tolyl)silyl]ethane at Cu electrodes.^{35,71}



Optimisation of this process using various solvents (DME, MeCN, DME/DMF, DME/propylene carbonate) and various supporting electrolytes [Bu₄NBF₄, Bu₄NClO₄, Bu₄NOC(O)CF₃, Bu₄NBPh₄, LiCl] showed that the best conditions for polymerisation are created by conducting the process in DME/Bu₄NBPh₄.⁷¹ When a supporting salt incorporating a trifluoroacetate anion was used, chlorine in the initial chlorosilane molecules was found to exchange with fluorine.⁷¹

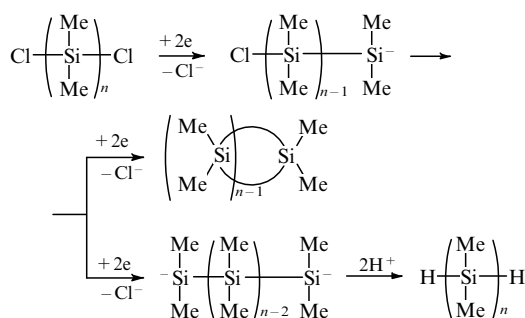
A series of studies have been devoted to electropolymerisation of dichlorodimethylsilane **4**.^{42,58,72} Umezawa *et al.*⁷² studied the influence of the conditions of electrolysis (ion-exchange membrane in a divided cell, metals and alloys of various purity grades as electrode materials) on the efficiency of electroreductive polymerisation. High yields of the products are achieved when the process is carried out in the DME/Bu₄NCl system in a diaphragmless cell with polarisation of Al electrodes by alternating current.

Since the reduction of chlorotriphenylsilane **2** in the presence of Me₃SiCl yields cross-disilane (*cf.* Refs 37, 49), while that in the presence of Me₂SiCl₂ yields a polymer containing both phenyl and methyl groups,⁵⁸ a nucleophilic rather than a radical mechanism for the formation of polysilane units has been assumed. It has been noted^{16,73} that dichloropolysilanes with longer chains are reduced at more positive potentials than short-chain polysilanes.[‡] Therefore, it has been assumed that polymerisation occurs *via* a nucleophilic attack by the monochloropolysilyl anion on the silicon atom in the initial molecule^{42,58,72} (*cf.* Ref. 56), according to the following scheme



Termination of the polymerisation chain was assumed to occur either *via* intramolecular nucleophilic attack yielding cyclic polysilane or *via* protonation.

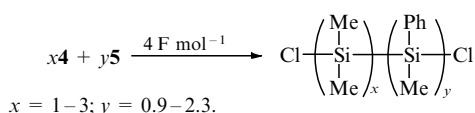
[‡] This regularity is apparently valid, taking into account the effects of σ -Si conjugation in polysilane chains;⁷⁴ however, judging from the potentials reported in one of these studies,⁷³ the researchers did not deal with the reduction of Si–Cl bonds.



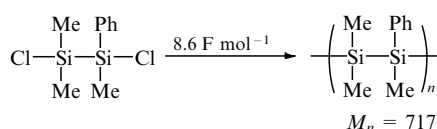
Therefore, in order to ensure initiation of the polymerisation and chain termination, it has been proposed to add to the electrolyte small amounts of a monochlorosilane (for example, Ph_3SiCl), which is reduced at less negative potentials than the dichlorosilane **4** forming the chain.⁷⁵

Dimethylpolysilane was prepared in a current yield of 72%–90% by electroreduction of dichlorodimethylsilane **4** without a solvent or with the addition of hexamethylphosphoric triamide (HMPT) or tris(3,6-dioxoheptyl)amine as a complex-forming agent in an undivided cell with a stainless-steel cathode and Al anode.⁷⁶ The highest yield is achieved when the mixture is treated with ultrasound with a frequency of 35 kHz.

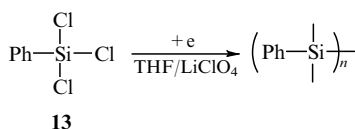
Electrosynthesis of heterosubstituted polysilanes by joint reduction of the dichlorosilanes **4** and **5** has been reported.⁴⁹ The composition of the polymer varies as a function of the ratio of the initial silanes.



A similar polymer has been obtained by electroreduction of 1,2-dichloro-1,1,2-trimethyl-2-phenyldisilane.⁵¹



Electroreduction of trichloro(phenyl)silane **13** in a THF/ LiClO_4 solution at a Mg electrode results in the formation of polysilanes with a two-dimensional structure of the silicon skeleton.⁷⁷ The electrolysis was carried out with ultrasonic treatment of the mixture and potential sweep from 0 to -3 V (vs Ag/Ag^+) during the process. The yield of the polymer ranged from 13% to 71%. The molecular weight of the resulting polyphenylsilane was estimated as $M = 5000-7100$.⁵⁶



A series of studies have been devoted to reductive polymerisation of polyfunctional silanes R^1SiX_3 , $\text{Cl}(\text{SiR}_2^1)_n\text{Cl}$, R^1SiCl_3 , SiCl_4 and $\text{ClR}^1\text{R}^2\text{SiR}^3\text{R}^4\text{X}$ ($\text{R}^{1-4} = \text{H, Alk, Ar, AlkO, NR}_2, \text{SiR}_3$) (see, for example, Refs 37, 78–81). This process giving rise to polysilane products is of interest as an alternative route for the synthesis of compounds used in the production of ceramic materials.

Poly(pentafluorophenylsilylene) has been synthesised by cathodic polymerisation of trichloro(pentafluorophenyl)silane.⁸²

In conclusion, it should be noted that studies on electroreduction of chlorosilanes are mostly synthetic. At present, there is scarcely any information on the kinetics and thermodynamics of the electron transfer and rupture of the $\text{Si}-\text{Cl}$ bond, and the conclusions about the nature of species resulting from the transfer

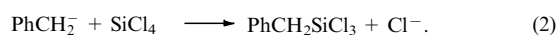
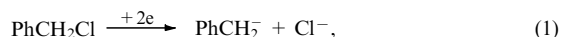
of electrons have been based on the structures of final products of electrolysis or on retro-synthetic analysis.

IV. Reactions of electrically generated nucleophiles with an electrophilic silicon atom

1. C-Nucleophiles

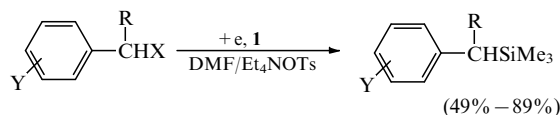
Electroreduction of organic compounds that are converted into carbanions by two-electron cleavage of the $\text{C}-\text{X}$ bond ($\text{X} = \text{H, Hal, OCR, OAc}$) is widely used in the preparative organic electrochemistry of silicon to synthesise various compounds with $\text{Si}-\text{C}$ bonds. In this case, the role of the electrode reduces to the generation of C^- -nucleophiles, which replace chlorine in chlorosilane molecules. It has been assumed that only relatively stable carbanions (All, Vin, Ar) are suitable for these reactions. Later, it has been found that when a soluble anode is used (Mg, Al, Zn, Cu) and the process is conducted in the presence of a complex-forming agent [DMF, HMPT, tetramethylurea, tris(3,6-dioxoheptyl)amine], electrically generated aliphatic carbanions can also be involved in the reaction.

Evidently, the first example of this type of synthesis is provided by the cathodic synthesis of benzyltrichlorosilane⁸³ by electrolysis of benzyl chloride in MeCN/ Et_4NCl at a Pb cathode in the presence of silicon tetrachloride (Eqns 1 and 2).

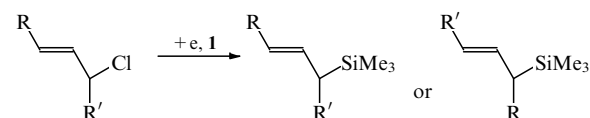
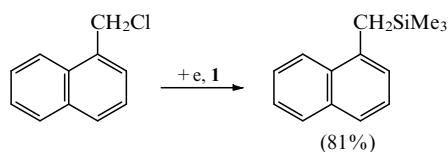


Benzyltrichlorosilane is formed in a substance yield of 19.1% and a current yield of 5%. When chlorosilane **1** is used instead of SiCl_4 ,^{59,84} this process gives benzyltrimethylsilane **20**.

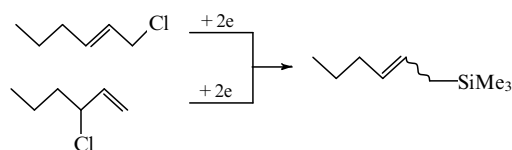
β -Silylated compounds with functionally substituted phenyl, naphthalene and alkenyl fragments were also obtained in good yields by a similar scheme.



$\text{R} = \text{H, Me};$
 $\text{X} = \text{Br, Cl};$
 $\text{Y} = \text{H, Me, MeO, CN, CO}_2\text{Me}.$



Isomeric allyl chlorides that differ in the position of the chlorine atoms in their molecules undergo cathodic silylation to give the same compound with a terminal Me_3Si group as the only product.⁵⁹

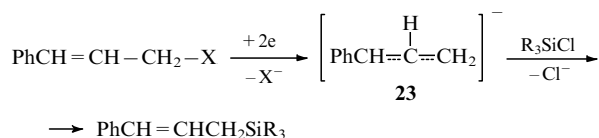


Chemical silylation with a Grignard reagent usually affords a mixture of products with inner and terminal Me_3Si groups.

Electroreduction of PhCH₂Cl, PhCl and PhBr in various solvents susceptible to complex formation [DMF, HMPT, (Me₂N)₂CO] in an undivided cell with a soluble Mg anode⁸⁴ leads to similar results. Carbanions resulting from electroreduction of allyl, vinyl, aryl and hetaryl halides (DMF/Et₄NOTs, divided cell, Pt electrodes) react with chlorosilanes **1**, **3** and **10** according to Eqns. (1)–(2) to give the corresponding organosilicon compounds⁸⁵ in preparative yields (47%–98%). Only chlorosilanes are suitable as silylating agents under these conditions; *O,N*-bis(trimethylsilyl)acetamide **21** and methoxytrimethylsilane **22** are inactive in this reaction.

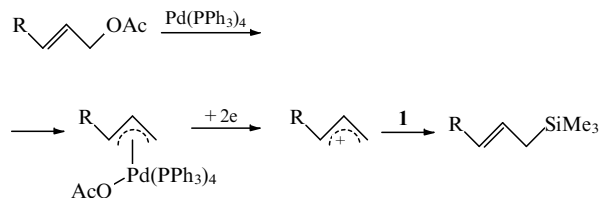
Aryl halides containing two different halogen atoms in their molecules (in particular, 4-bromiodobenzene) are selectively silylated with the chlorosilane **1** at the C–I bond thus yielding (4-bromophenyl)trimethylsilane.⁸⁶

Cinnamyltrimethylsilane can be obtained by electrosynthesis not only from cinnamyl chloride but also from other cinnamyl derivatives. In fact, the intermediates of reductive decarboxylation of cinnamyl acetate are converted into a silylated product in a yield of 25%–50%. Cinnamyl carbonate and cinnamyl sulfone can be converted into the same product in lower yields.⁸⁶ Evidently, this process occurs according to the following general scheme that includes formation of allylic anionic intermediate **23**:

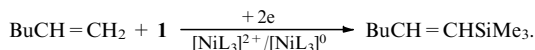
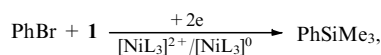


X = Cl, OAc, OCO₂Me.

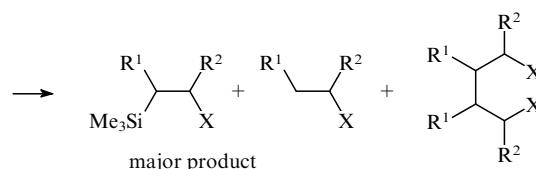
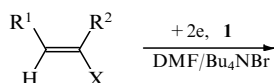
Allyltrimethylsilanes have also been obtained by homogeneous reduction of allyl acetates with Pd(PPh₃)₄ in the presence of an excess of chlorotrimethylsilane.⁸⁷ This reaction yields an inner alkene as the major product. This has been suggested to be due to the fact that the chlorosilane attacks the electrically generated carbanion from its sterically less shielded side.



Electrocatalytic reduction of PhBr and hex-1-ene with the [NiL₃]⁰ complex (L is 2,2-dipyridyl, PPh₃) in the presence of the silane **1** also affords cross-coupling products.¹⁰

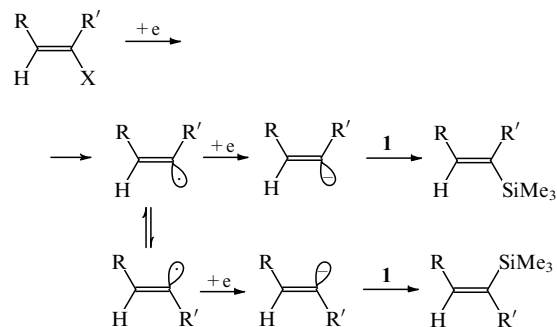


Electroreductive silylation of α,β-unsaturated esters, nitriles or ketones in an undivided cell with a Mg, Al or Zn anode results in the formation of the corresponding β-silyl derivatives (β-silyl propionates, nitriles or ketones).⁸⁸ When this process is conducted with a graphite or Pt anode, it gives no silylation products.



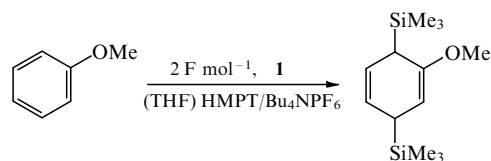
X = CO₂Et, CN, COMe.

When individual (*E*)-vinyl halides are introduced in this reaction, mixtures of (*E*)- and (*Z*)-isomers of vinyl silanes are always formed. Disubstituted (*E*)-vinyl halides yield mostly silylated (*Z*)-derivatives. This isomeric distribution is due to the fact that the following equilibrium involving the intermediate vinylic radical is established.

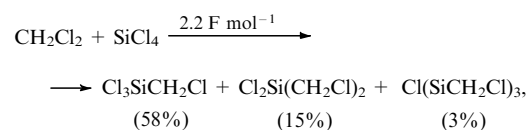


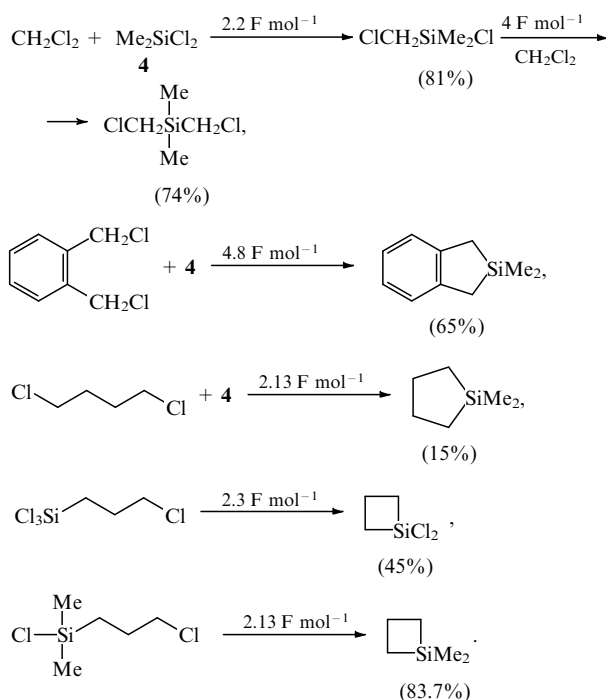
Since the (*E*)-radical is more stable than the (*Z*)-radical, it is the former that is reduced predominantly to give an (*E*)-vinylic anion; this anion reacts with **1** yielding (*Z*)-vinylsilane. A similar *cis-trans* isomerisation of the radical controls the stereochemistry of silylation of halostyrenes (Hal = I, Br, Cl).⁸⁶ Since the potential for the transfer of the second electron (*E*_{R·/R⁻}) does not depend on the nature of the halogen, whereas the reduction potential of the halide is, conversely, determined by the nature of the halogen (*E*_{C–I} > *E*_{C–Br} > *E*_{C–Cl}), the styryl radicals generated from the iodo-derivatives, for kinetic reasons, have more time to isomerise than those generated from the corresponding chlorides. Thus, the proportion of the *cis*-isomer varies in the opposite direction with respect to the ease of reduction of the halostyrene.

1-Methoxy-3,6-bis(trimethylsilyl)cyclohexa-1,4-diene, a precursor of ketoprofen, was prepared in a current yield of 70% by electroreduction of anisole (undivided cell, a stainless-steel cathode and an aluminium anode) in the presence of Me₃SiCl in a solution in THF/HMPT (4 : 1) or without THF but with addition of a complex-forming agent (HMPT).⁸⁹



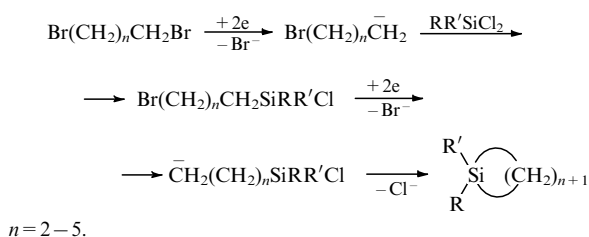
Based on an approach proposed in a series of studies,^{84, 85, 90–93} an electrochemical technique for the synthesis of carbosilanes, including cyclic ones, has been developed and described in a patent.⁹⁴



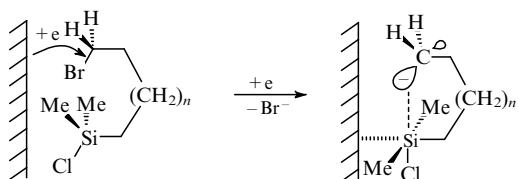


When this process is carried out with iodo-derivatives, the yields of the products are higher than in the case where bromides and chlorides are used.

Reduction of organic dihalides in the presence of Si-containing dichlorides under similar conditions^{95, 96} affords cyclic carbosilanes. Their yields (7%–91%) depend on the structure of the initial dihalide (the nature of the halogen and the length of the chain) and on the strain in the resulting ring. As the size of the ring increases, the yield of the reaction product first increases, reaches its maximum, as should have been expected, for 5- and 6-membered rings and then diminishes. The yields of cyclic disilanes depend also on the concentration of the halogenated substrates and on the electrode potential; an increase in either of these parameters leads to a decrease in the yields of silacycloalkanes.



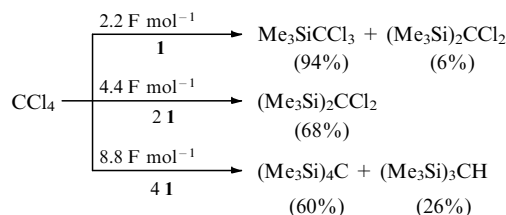
It is assumed that at the step of the linear silylated intermediate,⁹⁵ an orienting influence of the cathode is manifested; owing to this influence, silicon assumes a penta- or hexa-coor-dinated configuration favourable for the intramolecular nucleophilic attack.



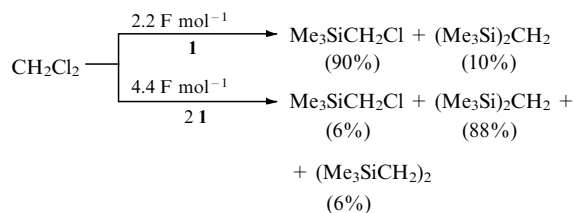
Electroreduction of 1,4-dibromobutane in the presence of tetrachlorosilane at a 1,4-dibromobutane : tetrachlorosilane ratio of 2:1 permits preparation of a bicyclic product, 5-sila-spiro[4.4]nonane, in a yield of 24%.

Electroreductive silylation of CCl_4 , CHCl_3 and CH_2Cl_2 ⁹⁰ is much more selective than the classical silylation. The use of soluble anodes made of various metals (Zn, Al, Mg), the cations

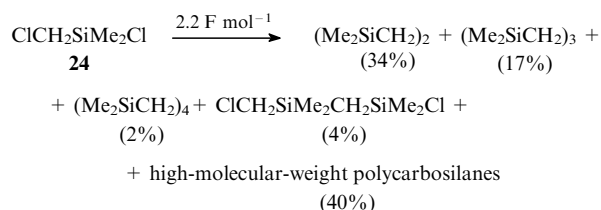
of which are reduced at different potentials, permits selective preparation of chlorine-containing products of partial silylation, the reduction potentials of which are more negative than those of the M^+ . For example, monosilylation of CCl_4 and $CHCl_3$ is carried out using a Zn anode, while disilylation occurs with a Mg anode and for trisilylation, an Al anode is used.



Mono- and disilylation of CH_2Cl_2 (Al anode) have been carried out in a similar way.^{57, 90}

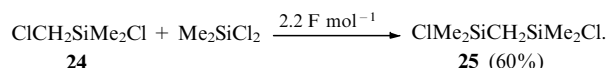


Under similar conditions, chloro(chloromethyl)dimethylsilane **24** is converted into a mixture consisting of cyclic 4-, 6- and 8-membered carbosilanes, a linear dimerisation product and polycarbosilanes^{26,69,91} (the yields were taken from Ref. 26).



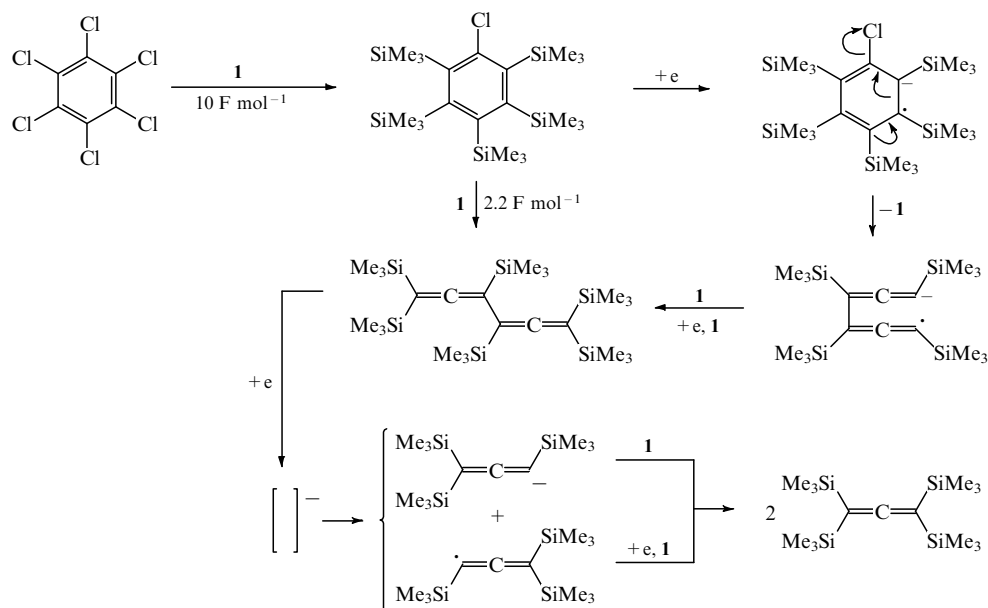
When a Mg anode is used (DMF/MgCl₂), the four-membered product is not formed.²⁶ It is of interest that the yield of the intermediate linear terminal dichlorocarbosilane increases from 4% to 43% when the solution is diluted 8-fold,^{26, 97} although this compound is formed by an intermolecular S_N2 mechanism and, hence, its proportion should have decreased following a decrease in the concentration.

The reduction of the chlorosilane **24** in the presence of dichlorodimethylsilane²⁶ (used as an electrophilic trap for the chlorodimethylsilyl carbanion) has given rise to bis(chlorodimethylsilyl)methane **25** in a preparative yield (60%). The high chemical selectivity of the process was achieved by maintaining the 1:1 ratio of the reactants during the electrolysis. For this purpose, Me₂SiCl₂ was gradually added to the reaction mixture, and its excess in the solution was thus avoided.

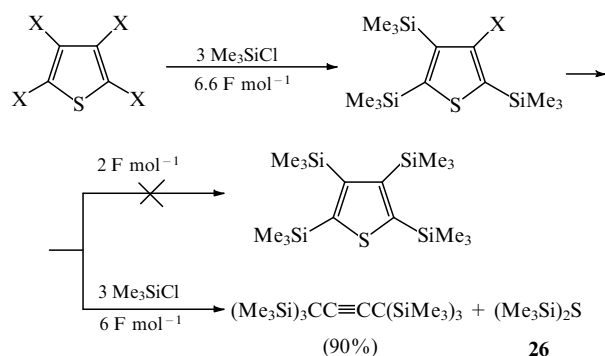


The electroreduction of benzal chloride in DMF/LiClO₄ in the presence of the chlorosilane **1** results in the formation of (α -chlorobenzyl)trimethylsilane or geminal benzaldisilane, depending on the amount of electricity passed.⁹⁸ Since the reduction potential of the dihalide is 560 mV more positive than that of the (α -chlorobenzyl)silane, the reduction of the latter yielding benzaldisilane starts only when the initial dichloride has reacted almost completely. Chromatographic monitoring of the process makes it possible to stop the reaction at the stage of monosilylation and thus to obtain the product in 57%–98% yield. The subsequent electrolysis affords the disilylated product (yield 72%–91%). When a stainless-steel cathode is used, the yields of mono- and

Scheme 1

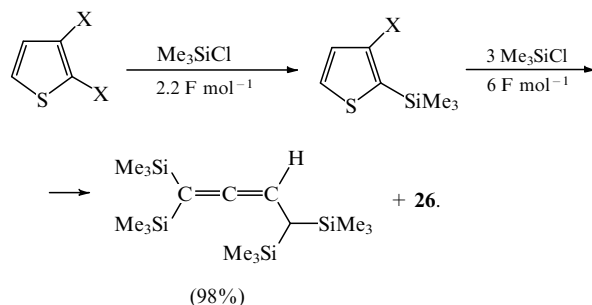


Cleavage of the ring in tetrahalothiophene is accompanied by the formation of hexamethyldisilathiane **26**.



X = Br, Cl.

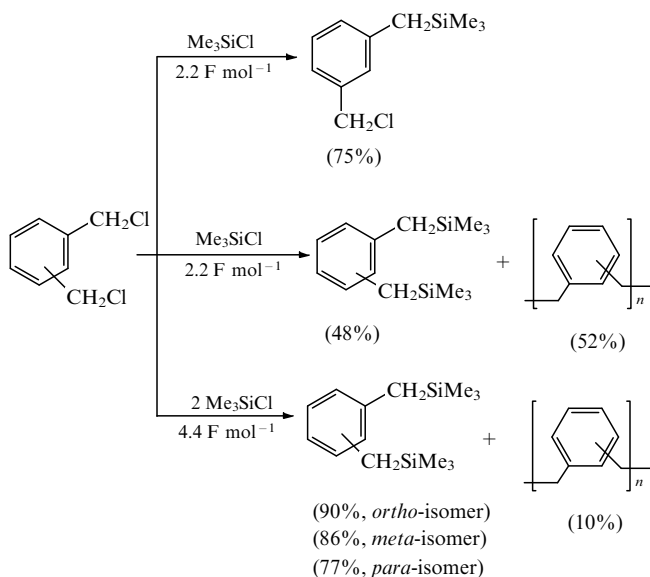
Silylation of 3-halo-2-trimethylsilylthiophene also yields products of ring opening in almost quantitative yield.



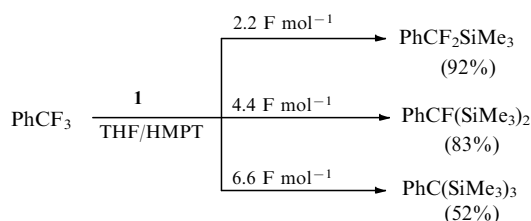
Using the correlation between the reduction potentials (E_p) of 1-R-3,4-dichloro- or 4-R-1,2-dichlorobenzenes and the sum of the σ_m and σ_p constants of substituents, it has been shown that substituents for which the $\sigma_m - \sigma_p > 0$, direct silylation to the *meta*-position, while those with $\sigma_m - \sigma_p < 0$ lead to *para*-silylation.

An interesting regularity has been observed in the silylation of disubstituted chloromethylbenzenes. Only *meta*-derivatives undergo monosilylation, whereas *ortho*- and *para*-isomers afford no monosilylation products.¹⁰¹ When 2.2 F mol⁻¹ of electricity is passed, the latter are immediately converted (by approximately 50%) into disilylated derivatives. It has been assumed that this is

due to the intermediate formation of *o*- or *p*-xylylene, which is converted into the corresponding polymer in 52% yield.

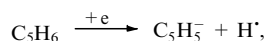


Silylation of the C–F bond in trifluoromethylbenzene carried out under the same conditions¹⁰² permits preparation of any of the three possible products by passing the appropriate amount of electricity (chromatographic yields are presented).

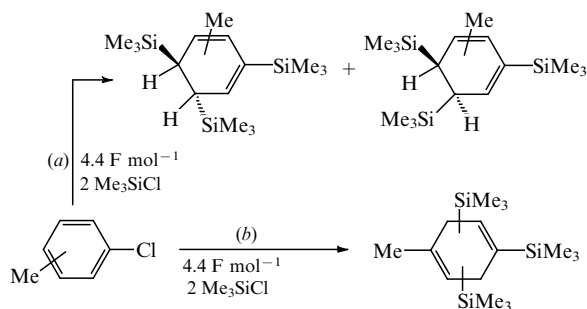


Synthesis of trimethylsilylcyclopentadiene (in a current yield of 96% based on the single-electron process) by the reaction between the electrically generated cyclopentadienyl anion and the chlorosilane **1** has been reported.¹⁰³ Cyclopentadiene was reduced at a Fe cathode in a divided cell in MeCN in the presence of Et₄NBr. Then a solution of the chlorosilane **1** in MeCN was added to the resulting catholyte (the solution contained some NaBr

added in order to shift the equilibrium in the reaction between $C_5H_5^-$ and **1** through binding the liberated chloride anion into insoluble NaCl).



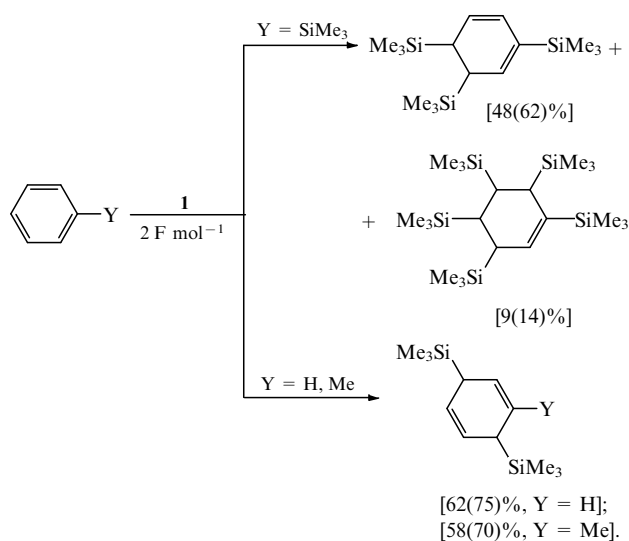
A reduction of monochlorotoluenes in the presence of the chlorosilane **1**, more extensive than the two-electron reduction, involves the aromatic ring and leads to the loss of aromaticity.^{76, 92}



(a) *ortho*- and *meta*-isomers, (b) *para*-isomer.

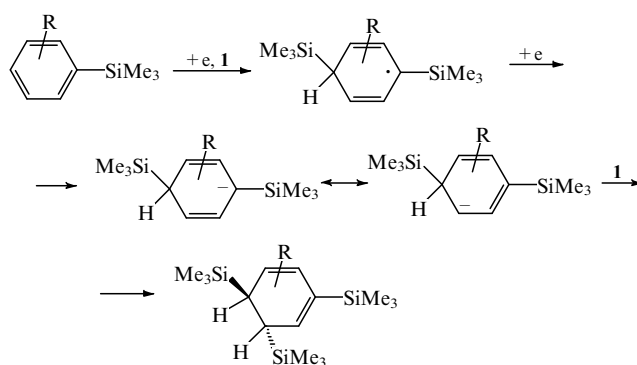
trans-Isomers predominate in the product mixture. When the DMF/MgCl₂/Mg system is used, only bromobenzene is silylated.

The nature of the unsaturated products resulting from silylation of aromatic compounds depends on the structure of the initial compound (chromatographic yields are given in parentheses).⁹²

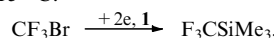


Benzene and toluene are converted into bis(trimethyl-silyl)cyclohexa-1,4-dienes. In the case of benzene, a 7 : 3 mixture of *trans*- and *cis*-products was obtained, while toluene gave only the *trans*-isomer.

Chemical silylation of systems of this type yields at once pentakis(trimethylsilyl)cyclohexanes, whereas electrochemical silylation can be selectively terminated when tris(trimethylsilyl)-containing conjugated dienes have been formed. The stereochemical control of the electrosilylation of aromatic systems is due to the steric effect of the first trimethylsilyl group entering the molecule. In fact, the second silylation occurs from the less shielded side of the molecule. This attack affords the kinetically controlled product; in the case of *trans*-isomer, this is also the thermodynamically controlled product.⁹²



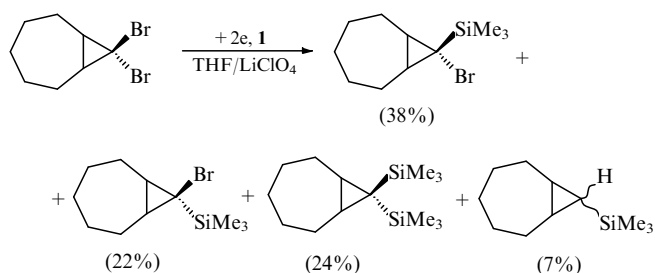
The electrochemical method for the synthesis of Ruppert's reagent was proposed in two publications at almost the same time.^{104, 105} In these studies, CF₃Br served as the source of the CF₃ group; the solution was saturated with this compound at -30 to -15 °C.



The authors of both studies advise the same electrodes (an Al anode and a Ni cathode) but different solvents and supporting electrolytes [DMF/Bu₄NBr¹⁰⁴ and PhOMe:HMPT (10 : 1)/Bu₄NPF₆¹⁰⁵].

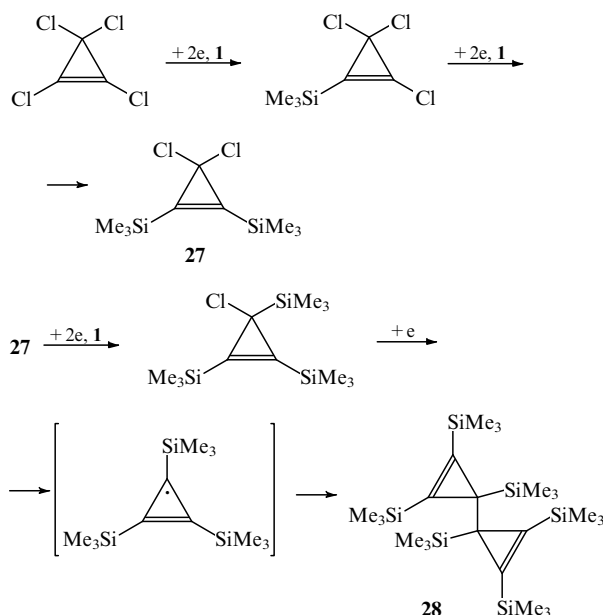
It is of interest that together with F₃CSiMe₃, 10%–15% of hexamethyldisilane is formed,¹⁰⁵ although the chlorosilane **1** is not yet reduced at the potential of electrolysis. It was assumed that the disilane is formed from the Si–Br derivative, which appears in the mixture *via* the Br/Cl exchange accelerated by Al³⁺ ions.

Successive substitution of the Br atoms in 1,1-dibromocyclopropanes by Me₃Si groups has been accomplished by electroreduction of this compound in the presence of the chlorosilane **1**.¹⁰⁶ The same process involving 8,8-dibromobicyclo[5.1.0]octane affords various silylated derivatives with moderate selectivity.¹⁰⁷ In addition to the silylated products, 10% of the unreacted initial dibromide was detected in the product mixture. Ultrasonic treatment of the reaction mixture doubles the apparent current yield. Since the process was carried out with a Mg anode, it was assumed that in this case, the silylated product has also been formed in a competing purely chemical (sonochemical) reaction with the participation of Mg.



Since sonochemical processes usually stop at the monosilylation stage, the electrochemical version yielding disilylated products is a convenient method for the synthesis of these cyclopropane derivatives.¹⁰⁷

Successive reduction of tetrachlorocyclopropene in the presence of the chlorosilane **1** made it possible to prepare its mono-,¹⁰⁸ di- and trisilylated derivatives.¹⁰⁹ When this process was carried out in the THF/HMPT (10 : 1) system using a Ni cathode, an Al anode and 8 F mol^{−1} of electricity, hexakis(trimethylsilyl)-3,3'-bi(cyclopropenyl) **28** was obtained in 40% yield; silylated dichloropropene **27** was formed simultaneously.



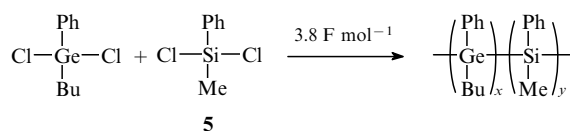
When a Mg anode is used, compound **28** is scarcely formed.¹⁰⁹

Thus, the reduction of a C–Hal bond is, obviously, the most convenient method for the electrical generation of C-nucleophiles, because most organic halides are reduced at less negative potentials than chlorosilanes. Generation of a carbanion by reduction of a C–H bond requires more negative potentials and it often can be accomplished only at cathodes made of transition metals.¹⁰³ The reduction of aromatic systems is accompanied by their degradation; however, this process can be used for electrosynthesis of silylated dienes and alkenes, which are of interest for Diels–Alder reactions.

2. Organoelement nucleophiles

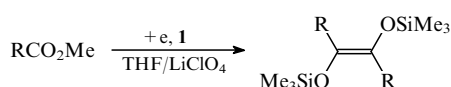
This Section deals with processes consisting of electrical generation of nucleophiles based on Ge^- , Sn^- , O^- , N^- , S^- , Se^- and so on, *i.e.* elements other than carbon, and their subsequent reactions with reagents containing electrophilic silicon, most frequently, with the chlorosilane **1**.

Electroreduction of chlorotrimethylgermane¹¹⁰ in the presence of the chlorosilane **1** (Mg anode and Mg cathode, THF/ LiClO_4) affords a heteroelement dimer containing a Ge–Si bond, whereas its reduction in the presence of the dichlorosilane **5** gives rise to a heterocopolymer.

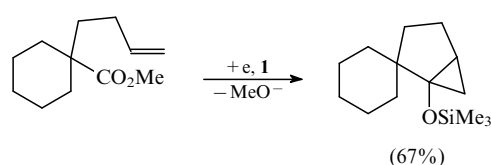


Reduction of tributylchlorostannane in the presence of the chlorosilane **1** under similar conditions and at ratios of the initial chlorides of 1:1, 1:5 and 1:10 leads to tributyl(trimethylsilyl)stannane (10%, 35% and 50%) and hexabutylstannane (59%, 55% and 41%, respectively).²⁹

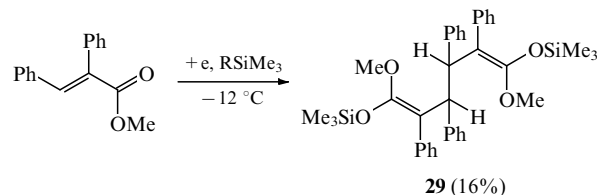
Esters of carboxylic acids^{50, 111, 112} are reduced with Mg electrodes (anode and cathode) in an undivided cell in the presence of Me_3SiCl to give products of the acyloin condensation.



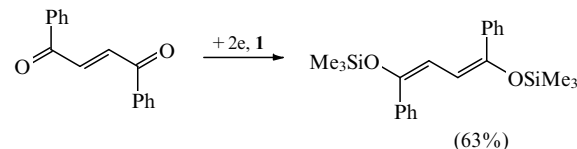
The same process involving an unsaturated ester that has a more positive reduction potential than the chlorosilane **1** results in the formation of a bicyclic spiro-compound.¹¹³



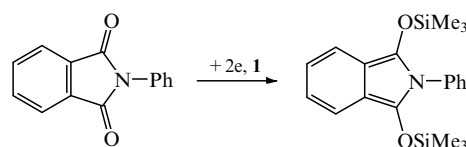
Electroreduction of unsaturated carbonyl compounds under aprotic conditions in the presence of *O,N*-bis(trimethylsilyl)acetamide **21** or the chlorosilane **1** affords products identified as silyl ethers.¹¹⁴ It is of interest that acetamide **21** is inactive in the reaction with C-nucleophiles^{85, 86} but reacts with the O-nucleophile to give dimeric trimethylsilyl unsaturated diether **29**.



The product of two-electron reduction of 1,2-dibenzoyl ethene attacks nucleophilically the chlorosilane **1** to give 1,4-diphenyl-1,4-bis(trimethylsilyloxy)buta-1,3-diene.

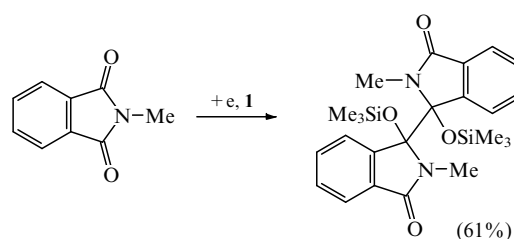


2-Phenyl-1,3-bis(trimethylsilyloxy)isoindole has been prepared by two-electron reduction of *N*-phenylphthalimide in MeCN/ Et_4NCl in the presence of the chlorosilane **1**.¹¹⁵



The resulting isoindole was not isolated in a pure state owing to its high sensitivity to moisture and air; however, this compound is quite stable in a catholyte under a layer of dry argon and can be trapped by an appropriate dienophile after the electrolysis.¹¹⁵

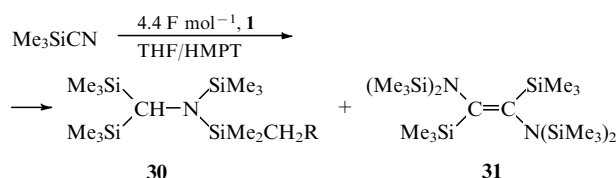
Single-electron reduction¹¹⁵ of *N*-methylphthalimide under the same conditions yields a dimeric silylated bis-lactam.



This process is assumed to include the formation of a radical anion, which is able either to react directly with an electrophile in two $\text{E} + \text{C}_{\text{S}_\text{N}2}$ steps (two-electron process) or to undergo dimerisation followed by silylation to give the bislactam (single-electron process).

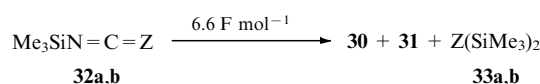
Electroreduction of acylimidazoles in the presence of the chlorosilane **1** gives rise to acylsilanes¹¹⁶ including those containing Cl and C(O)OAlk groups.

The products of electroreduction of Me_3SiCN react with the chlorosilane **1** affording silylated products **30** and **31**, the protolysis of which makes it possible to synthesise bis(trimethylsilyl)-methylamine.¹¹⁷

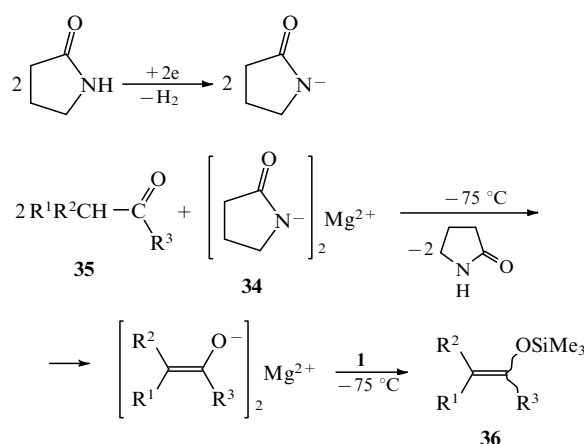


R = H, Cl.

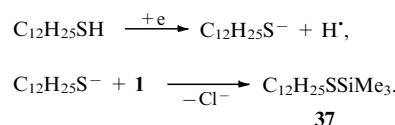
The same products, together with tris(trimethylsilyl)amine **33a** and hexamethyldisiloxane **33b** were obtained by electrochemical silylation of trimethylsilylcarbodiimide (Z = NSiMe₃) **32a** and trimethylsilyl isocyanate (Z = O) **32b**.¹¹⁷



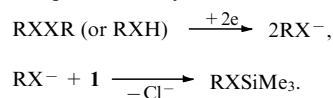
Magnesium salt **34** prepared by electroreduction of 2-pyrrolidone in an undivided cell with a soluble Mg anode¹¹⁸ has been used as an electrically generated base for functionalisation of carbonyl compounds. Thus the magnesium enolate formed upon addition of ketone **35** to two equivalents of the electrically generated base at a low temperature reacts with the chlorosilane **1** to give enoxysilane **36**; *N*-trimethylsilyl-2-pyrrolidone is formed as a side product.



Magnesium thiolate electrically generated upon reductive rupture of the S–H bond in dodecanethiol¹¹⁹ reacts with the chlorosilane **1** to give thiosilane **37** in a current yield of 78%.



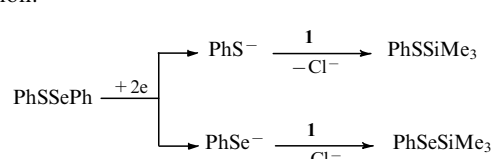
Reduction of diorganodisulfides and -diselenides as well as thio- and seleno-phenols (in the two latter cases, a Fe cathode is used) carried out in the presence of mono- and dichlorosilanes^{63, 120, 121} gives rise to the corresponding thio- and selenosilanes in good preparative yields (60%–87%). Chromatographic analysis of reaction mixtures shows that the reaction proceeds almost quantitatively.



R = Ar, Alk; X = S, Se.

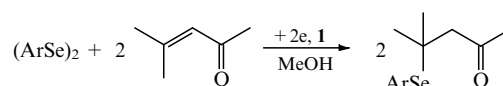
By means of an electrochemical variant of the method of competing reactions in the classical and reversed schemes (Scheme 2), it has been shown that the rates of *S_N2* reactions of electrically generated PhS[−] and PhSe[−] anions with chlorosilanes (Me₃SiCl, MeVinSiCl₂, Me₂SiCl₂ and SiCl₄) are related as 1 : 1.97 : 2.34 : 4.61 and 1 : 1.45 : 2.5 : 4.1, respectively. The rate of

nucleophilic selenation is 9.3 times higher than the rate of thiolation due to the higher nucleophilicity of the Se-containing anion.¹²²



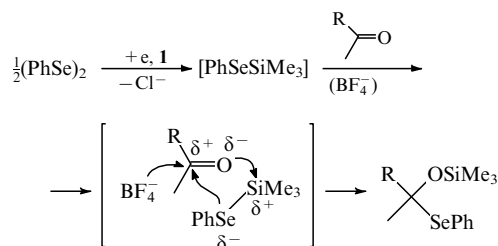
Scheme 2

Cathodic arylselenation of α,β-unsaturated carbonyl compounds has been described. It was assumed that trimethylsilyl selenide resulting from interaction of the electrically generated ArSe[−] anion with the chlorosilane **1** participates in the process.¹²³ Methanolysis of the silyl selenide yields arylselenol, and the latter acts as the reactive intermediate in this *in situ* silylation of enones.

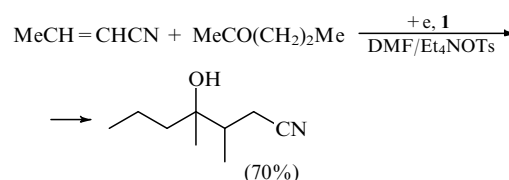
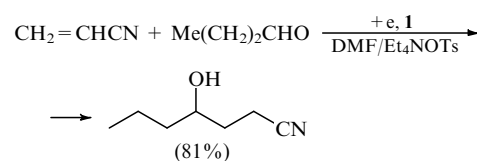
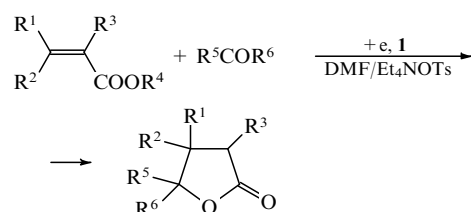


Electrically generated silyl chalcogenides have been used for functionalisation of carbonyl compounds (Scheme 3).^{121, 124–128}

It is assumed that the addition of selenosilane to the C=O bond under the conditions of electrolysis involves anionic catalysis by the anion of the supporting electrolyte.^{121, 129}

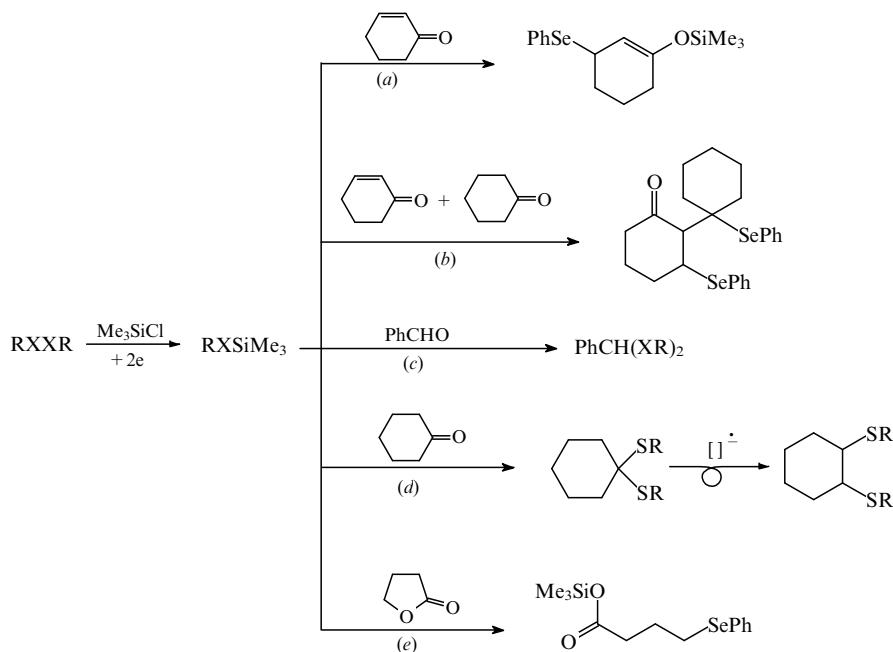


Electroreductive cross-hydrocoupling of α,β-unsaturated esters with aldehydes or ketones²⁸ in the presence of the chlorosilane **1** results in the formation of γ-lactones in good yields (51%–86%). Similarly, α,β-unsaturated nitriles are converted into γ-hydroxynitriles.



Although the molecules of the reaction products do not contain Me₃Si groups, the presence of the chlorosilane **1** is necessary, because coupling does not occur without it. The mechanism of the process has not been studied in detail; however, it is assumed that **1** is coordinated to the carbonyl compound thus activating the carbonyl group. Then this complex reacts with the radical anion resulting from single-electron reduction of the acrylate.

Scheme 3



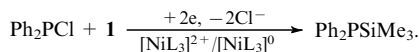
(a, b) X = Se; R = Ph; divided cell;

(c) X = S, Se; R = Et, Ph; divided cell;

(d) X = S; R = Et, Ph; one-compartment cell, Al(Mg) anode;

(e) X = Se; R = Ph; one-compartment cell, Al(Mg) anode.

Electrocatalytic reduction of Ph_2PCl by the complex NiL_3 (L is 2,2-dipyridyl or PPh_3) in the presence of the chlorosilane **1** yields diphenyl(trimethylsilyl)phosphine.¹⁰



V. Reduction of other classes of organosilicon compounds

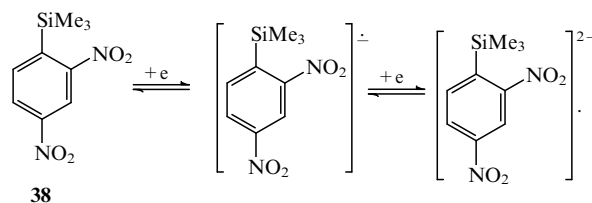
The interpretation of the stabilising influence of the silicon atom on radical-anion intermediates has changed following the evolution of the views on the electronic effects of silicon-containing substituents (from the idea that electron-withdrawing properties of α -silyl substituents are associated with participation of the vacant $3d$ orbitals of silicon atoms to the concept rejecting this participation¹³⁰ and based on the acceptor hyperconjugation interactions of σ^* orbitals). At present, none of the theoretical concepts can fully explain the experimental data on the electronic effects of silyl substituents. The concept according to which the overall influence of a silyl substituent on the energies of frontier molecular orbitals (FMO) is determined by a combination of various electronic interactions¹³¹ — inductive effect ($+I$), σ, π and σ, π^* -conjugation, mixing of the $\sigma_{(\text{Si}-\text{C})}$ and $3d$ orbitals of Si, mixing of d, σ^* orbitals with σ, π^* and σ, π orbitals and the formation of LUMO (d, π^*) — should be regarded as the most comprehensive (but also the most complex).

Since the $3d$ -orbital hypothesis (see Refs 130 and 131) agrees qualitatively with general quantum-mechanical views on intramolecular electronic interactions and with statements of the general concept¹³¹ (this hypothesis has been used in a number of original studies), we decided not to introduce the more recent interpretation but to remain within the framework of the $d_\pi-p_\pi$ -conjugation concept used by the researchers cited (see, for example, Refs 132–134).

The results of reversible polarographic reduction of 4-trimethylsilyl- and 4,4'-bis(trimethylsilyl)biphenyls ($E_{1/2} = -2.03$ and -1.94 V vs Hg pool, respectively),¹³² and of a number of

trimethylsilyl-substituted polyphenyls¹⁵ have been used to estimate the ϵ_{LUMO} values, which proved to be close to the ϵ_{LUMO} values obtained using EPR data. Interpretation of the spectra of the radical anions in terms of a model involving d orbitals of silicon made it possible to calculate the multiplicity of the C–Si π -bond, which was found to be approximately 0.18 in all the aromatic compounds studied.

The potentials of the reduction peaks (DMF/ Bu_4NClO_4 , Pt) of *o*-, *m*- and *p*-nitrophenyltrimethylsilanes ($E_p = -1.62$, -1.50 and -1.26 V vs SCE, respectively)¹³³ are several tens of millivolts more positive than the reduction potentials of the corresponding toluene derivatives. The radical anions formed upon the transfer of a single electron are quite stable ($i_a/i_k \cong 1$); however, although the process is reversible, $\Delta E_p/\Delta \lg(v) = 400$ mV for potential sweep rate v ranging from 40 to 400 mV s^{-1} . The reduction of 2,4-dinitrophenyltrimethylsilane **38** is characterised by two reversible peaks and occurs according to the equation



The stabilising influence of the trimethylsilyl group on the radical anion was explained¹³³ by the $d_\pi-p_\pi$ -conjugation of the Si atom with the aromatic ring.

The possible structures of the radical anions derived from *p*- and *m*-trimethylsilylnitrobenzenes have been discussed;¹³⁴ the distribution of the electron density in these species during the reduction was elucidated by EPR.

It has been reported¹³⁵ that α -silyl aryl ketones have lower reduction potentials ($\Delta E_{1/2} = 270$ mV) than their carbon analogues and that the energies of charge transfer in the π -complexes of α -silyl aryl ketones with tetracyanoethylene are higher than those in the complexes of carbon derivatives.

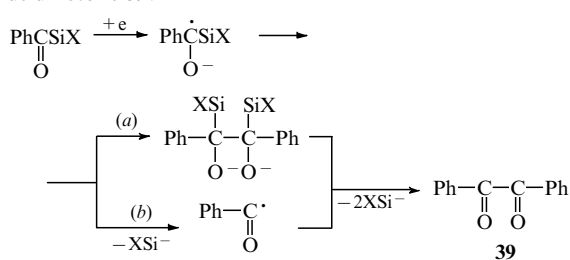
The polarogram of reduction of 5,5-dimethyl-5,10-dihydrodi-benzo[*b,e*]silinone ¹³⁶ exhibits two waves typical of ketones. The first wave ($E_{1/2} = -1.64$ V vs Hg pool, $\Delta E_{3/4-1/4} = 60$ mV) corresponds to the formation of a radical anion; the second wave is irreversible ($E_{1/2} = -2.27$ V, $\Delta E_{3/4-1/4} = 90$ mV). The decrease in the splitting constants in the EPR spectra attests to a decrease in the spin density in the benzene rings, which is due to the electron-withdrawing influence of the silicon atom.

The slight differences between the reduction potentials of 4-biphenyltrimethylsilane ($E_{1/2} = -1.948$ V vs Hg pool) and 4,4'-bis(trimethylsilyl)biphenyl ($E_{1/2} = -1.856$ V) and between those of bis(4-biphenyl)dimethylsilane ($E_{1/2} = -1.904$ V) and 4,4'-bis(4-biphenyldimethylsilyl)biphenyl ($E_{1/2} = -1.801$ V) have been attributed ¹³⁷ only to the effect of the second silicon atom, participation of the *d* orbitals of silicon in the transfer of conjugation between the benzene rings being completely ruled out.

Contrary to this and also to the conclusion made by Makarov and Kazakova ¹³⁸ that the unpaired electron in the radical ions derived from phenylsilanes is not delocalised through the SiMe₂ bridges, Il'yasov *et al.* ¹³⁹ have found, based on the EPR spectra of the electrically generated radical anions Ph₄Si^{•-}, that the unpaired electron does interact with all the phenyl groups.

Reduction of mono- and bis-trimethylsilyl-substituted naphthalenes ¹⁴⁰ occurs by a mechanism typical of reduction of aromatic hydrocarbons with reversible electron transfer giving a radical ion; in this case, the $E_{1/2}$ potentials are more positive than those for reduction of compounds with *tert*-butyl substituents ($\Delta E_{\text{SiMe}_3-\text{CMe}_3} = 220-290$ mV), which is a result of the simultaneous influence of two opposite effects: +*I* effect of the Me₃Si group and the electron-withdrawing effect of vacant 3*d* orbitals of Si on the π -system of the ring.

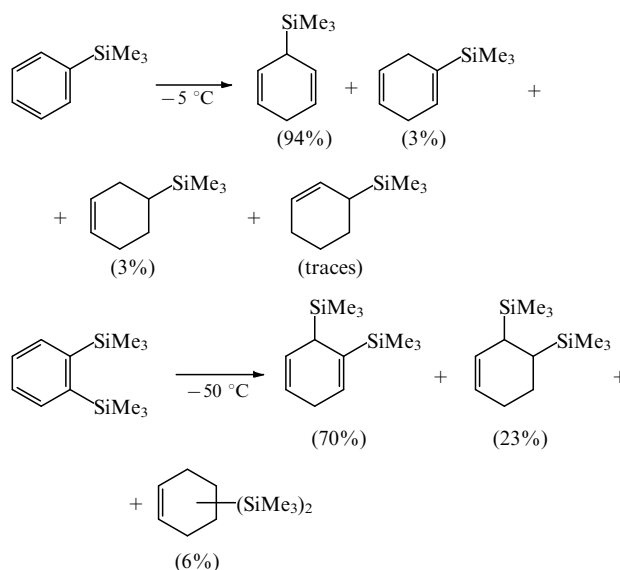
The reduction of a number of benzoylsilanes substituted in the ring in MeCN/Bu₄NClO₄ at a glassy carbon electrode involves the formation of a relatively unstable radical anion, which was detected at -80 °C by EPR. ¹⁴¹ At room temperature, the process is irreversible and, unlike the electroreduction of arylketones which affords pinacols, it occurs according to Scheme *a* or *b* and yields diketone **39**.



X = PhMe₂.

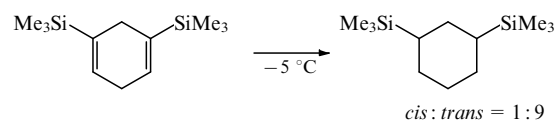
The potentials of the two reversible steps of electroreduction of 2,5-bis(trimethylsilyl)-1,4-benzoquinone ($E_{1/2} = 0.04$ and -0.51 V vs Hg pool; MeCN/Bu₄NI) are 200 mV more positive than the potentials of electroreduction of the corresponding di-*tert*-butyl derivative, ¹⁴² which is due to the electron-withdrawing influence of the Si atom (the mechanism of $d_{\pi}-p_{\pi}$ -conjugation).

Electroreduction of aryltrimethylsilanes in MeNH₂/LiCl at a Pt electrode in an undivided cell is a promising method for the synthesis of trimethylsilyl-substituted cyclohexa-1,4-dienes. ^{143, 144} This reaction is assumed to proceed as an electrochemical variant of the Birch reaction with participation of the metallic lithium resulting from the cathodic reduction of Li⁺. With substituents occupying various positions in the aromatic ring, the nature of the products is determined by steric and electronic interactions.



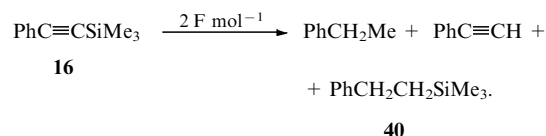
In addition to the products mentioned above, disilylated cyclohexenes with a different position of trimethylsilyl groups are formed in 6% yield.

It is noteworthy that at potentials more negative than reduction potentials of arylsilanes, electroreduction of silylated alkenes can also be achieved. ¹⁴⁴



Rupture of the double bond during the reduction of 6-trimethylsilylhept-6-en-2-one and intramolecular cyclisation lead to *cis*-1-methyl-3-trimethylsilylcyclohexanol. ¹⁴⁵

Reduction of trimethyl(phenylethynyl)silane **16** ($E_{1/2} = -2.02$ V vs Hg pool; DMF/Bu₄NI ¹⁴⁶) in an undivided cell in MeNH₂/LiCl at a Pt electrode requires 2F mol⁻¹ of electricity and affords a mixture of products that contains ethylbenzene (38%), phenylacetylene (47%) and trimethyl(2-phenylethyl)silane **40** (13%). ¹⁴³ The reduction occurs presumably *via* the formation of trimethyl(phenylethynyl)silyl radical anion [**16**]^{•-}, which undergoes either fragmentation at the C–Si bond (in MeNH₂) or protonation with retention of the C–Si bond (in the presence of PrⁱOH). In the latter case, compound **40** is formed in a markedly higher yield (31%).



The $E_{1/2}$ values for the reversible reduction of silylbutadienes have been reported. ¹⁴⁷ Since the interactions of silyl-substituted unsaturated compounds in excited states cannot be measured directly, some correlations were made on the assumption that the $E_{1/2}$ potentials of reversible electron transfer reflect the relative LUMO energies in neutral π -electron systems in the ground state. Thus the +*I* effect of the Me₃Si group dominating in the ground state is replaced by $d-\pi^*$ interaction at the singly occupied molecular orbital (SOMO) of the radical anion, and the sequence of potentials of di(trimethylsilyl)-substituted butadienes [$E_{1/2}$ for 1,4-, 1,3-, 1,2- and 2,3-bis(trimethylsilyl)butadienes are -1.80 , -1.85 , -1.90 and -2.13 V, respectively, with respect to the Hg

pool] is consistent with the sequence expected according to the theory of FMO with first-order perturbations ($1,4- < 1,3- \sim 1,2- < 2,3$ -isomers). Moreover, the electrically generated radical anion from 1,4-bis(trimethylsilyl)butadiene is so stable that its EPR spectrum can be observed at room temperature. Splitting constants indicate that the spin density of the radical anion is partly delocalised to the Me_3Si group.¹⁴⁷

Polarograms of silaacenaphthenes, 2-silaphenalanenes and 1,3-disilaphenalanenes and the EPR spectra of the corresponding electrically generated radical anions have been studied.¹⁴⁸ Since the molecules of these compounds are fairly strained, stability of their radical anions is lower than that of the radical anions derived from other silicon-containing aromatic compounds of this series.

The results of the polarographic single-electron reversible reduction of phenyl- and naphthyl silyl ketones,¹⁴⁹ vertical ionisation potentials (IP) and the data of electronic spectroscopy indicate that $E_{1/2}$ of the reduction of silicon-substituted ketones are markedly lower than those of their carbon analogues ($\Delta E_{\text{Si-C}} \cong 250\text{--}270$ mV) and that electron-withdrawing substituents at the carbonyl carbon atom have a greater influence on the electrochemical reactivity than substituents at the *para*-position of the aromatic ring.

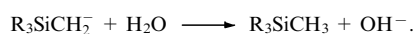
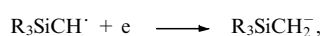
Phenyl-substituted polysilanes $\text{Ph}(\text{SiMe}_2)_n\text{Me}$ and $\text{Ph}(\text{SiMe}_2)_n\text{Ph}$ are reduced in the range of potentials $-3.3 < E_{1/2} < -3.2$ V, which is close to the region of electrical activity of the solvent [$E_{1/2} = -3.26$ V for *p*-bis(trimethylsilyl)benzene and $E_{1/2} = -3.23$ V for *p*-bis(pentamethylsilyl)benzene vs Ag/Ag^+], whereas naphthylpolysilanes exhibit one reversible diffusionally controlled wave ($n = 1$, $i/H^{1/2} = \text{const}$, where H is the height of the mercury column in the dropping-mercury electrode; $i/C = \text{const}$) or two single-electron reduction waves in an accessible range of potentials ($-2.845 \leq E_{1/2} \leq -2.781$ V vs Ag/Ag^+).¹³⁰ Since linear permethylpolysilanes $\text{Me}(\text{SiMe}_2)_n\text{Me}$ ($n = 2\text{--}5$) are not reduced,^{130,150} reduction of polysilylated aryl derivatives, evidently, involves one of the degenerate antibonding orbitals of the Ar group. The decrease in $E_{1/2}$ for silylnaphthenes was interpreted taking into account inductive, σ , π , and $d_\pi\text{--}\pi_\pi$ effects of the silyl substituent; the two former effects increase ϵ_{LUMO} , while the latter markedly decreases it.¹³⁰

Cyclic permethylpolysilanes $(\text{Me}_2\text{Si})_n$ ($n = 5\text{--}7$) are reduced in $\text{Me}_2\text{O}/\text{DME}$ (3:1) in the presence of Bu_4NClO_4 to give a radical anion, the EPR spectrum of which recorded at -120°C indicates that the unpaired electron is delocalised over all the Si atoms in the ring.¹⁵¹

The $\text{Si}_6\text{Me}_{11}$ anion is formed upon electroreduction of $\text{Si}_6\text{Me}_{12}$ in HMPT at -1.9 V and can react with various electrophiles;¹⁵² for example, its reaction with EtBr affords the corresponding ethylated product.

Tetraaryldisilenes are reduced irreversibly in the THF/ Bu_4NPF_6 system at less negative potentials ($E_p = -2.03$ to -2.2 V vs SCE) than dialkyldiaryldisilenes ($E_p = -2.6$ V). This is due to the fact that the two aromatic rings and the double bond in the molecules of tetraaryl-derivatives are nearly coplanar; as a consequence, π^* orbitals of the disilene and aromatic fragments are largely mixed and the LUMO energies of the molecules decrease.¹⁵³

In the reduction of iodomethylsilanes,^{154,155} the presence of a Me_3Si group also shifts the $E_{1/2}$ potential to less negative values (Table 5); the corresponding polarograms contain two single-electron diffusion waves rather than one two-electron wave as in the case of primary iodoalkanes. The process was assumed to correspond to the $E + E + C$ scheme.



In the case of $\text{Et}_2\text{SiMeCH}_2\text{I}$, the slope in the plot for the $E_{1/2}$ potential against the logarithm of the period of dropping in the

Table 5. Characteristics of electroreduction of iodo- and chloromethylsilanes in 57% EtOH/0.09 M KCl (the $E_{1/2}$ potentials are referred to SCE).^{154,155}

Halomethylsilane	$-E_{1/2}^1/\text{V}$	$-E_{1/2}^2/\text{V}$
$\text{Et}_3\text{SiCH}_2\text{I}$	1.54	1.72
$\text{CF}_3(\text{CH}_2)_2\text{SiMe}_2\text{CH}_2\text{I}$	1.33	1.54
<i>p</i> - $\text{FC}_6\text{H}_4\text{SiMe}_2\text{CH}_2\text{I}$	1.40	1.53
<i>p</i> - $\text{ClC}_6\text{H}_4\text{SiMe}_2\text{CH}_2\text{I}$	1.37	1.50
<i>m</i> - $\text{CF}_3\text{C}_6\text{H}_4\text{SiMe}_2\text{CH}_2\text{I}$	1.34	1.45
$\text{Et}_2\text{SiMeCH}_2\text{I}$	1.56	1.70
$\text{Pr}_2\text{SiMeCH}_2\text{I}$	1.60	1.76
$\text{Bu}_2\text{SiMeCH}_2\text{I}$	1.58	1.79
$\text{PhSiMe}_2\text{CH}_2\text{I}$	1.43	1.56
$\text{Me}_3\text{SiCH}_2\text{Cl}$	1.51 ^a	
$\text{ClMe}_2\text{SiCH}_2\text{Cl}$ (41)	1.48 ^a	

^a From Ref. 157.

dropping-mercury electrode (t_1) is $\Delta E_{1/2}^1/\Delta \lg(t_1) \cong 60$ mV, which corresponds to the transfer coefficient $\alpha \cong 0.5$.¹⁵⁴

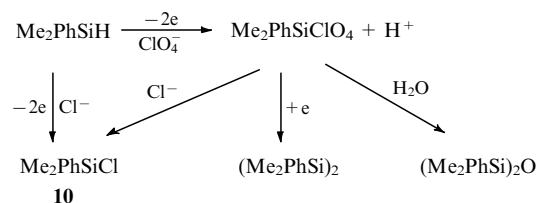
Using the method of homogeneous redox catalysis, it has been shown that the coordinate of the reaction of reduction of $\text{ClCH}_2\text{SiMe}_3$ **41** contains a point corresponding to the real radical anion.^{156,157} This mechanism of reduction, unusual for alkyl chlorides, is due to the fact that the negative charge arising on the α -carbon atom (more precisely, in the σ^* orbital of the C–Cl bond) upon electron transfer is delocalised by silicon, and this decreases the energy of the ground state of the radical anion, which thus becomes lower than the level of the transition state leading to dissociation. Due to the same effect, the E_p potentials of iodo- and chloromethylsilanes are abnormally small.

The reduction of Ph_3SiH and Ph_2MeSiH in the presence of Bu_4NClO_4 in a divided cell does not lead to the replacement of hydrogen by the halogen, as in the case of germanium analogues;¹⁵⁹ instead, it yields disiloxanes. When the electrolysis was carried out in the presence of Bu_4NBF_4 , formation of traces of Ph_3SiF was detected by GC/MS analysis, $(\text{Ph}_3\text{Si})_2\text{O}$ still being the main reaction product.

VI. Electrooxidation of organosilicon compounds

1. Hydrosilanes

Unlike oxidation of some hydrosilanes at metallic electrodes, which is characterised by low potentials (Table 6), oxidation of Me_2PhSiH at a glassy carbon electrode in $\text{MeCN}/\text{LiClO}_4$ occurs at a high potential⁸ $E_p = 2.2$ V vs SCE.¹⁶⁰ Preparative electro-oxidation of Me_2PhSiH in $\text{DME}/\text{Bu}_4\text{NClO}_4$ in the presence of CuCl_2 or CuCl gives rise to a number of products, the formation of which can be described by the following scheme:



Depending on the copper chloride used (CuCl_2 or CuCl) and on the amount of electricity passed, the chlorosilane **10** is formed in a yield of 46%–95%. Under the same conditions, $\text{Bu}^t\text{Me}_2\text{SiH}$ and Et_3SiH **42** are converted into the corresponding chlorosilanes

§ Since in the presence of CuCl , chloro-derivatives are also formed in a chemical process without passing the electricity, the high E_p values may be due to oxidation at these potentials of compounds other than hydrides.

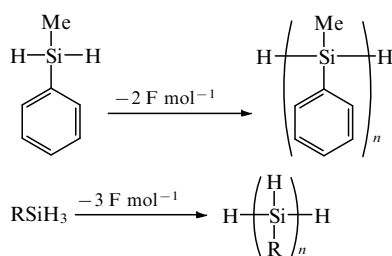
Table 6. Characteristics of electrooxidation of hydrosilanes.

Silane	E_p /V (vs SCE)	Electrode	i_k/i_a ($v = 0.5 \text{ V s}^{-1}$)	Ref.
Et ₃ SiH (42)	0.23	Pt ^a	0.63	161
(EtO) ₃ SiH	−0.05	Pt ^a	0.61	162
(EtO) ₃ SiH	0.45	Au ^a	0.42	162
(EtO) ₃ SiH	0.30	Hg ^a	0.34	162
MeCl ₂ SiH	−0.28	Pt ^b	0.9	163
MePh ₂ SiH	2.1	GC ^b	irrevers.	160
Me ₂ PhSiH	2.2	GC ^b	irrevers.	160
MePhSiH ₂	0.7	Pt ^c		164
PhSiH ₃	0.7	Pt ^c		164
<i>n</i> -C ₆ H ₁₃ SiH ₃	0.6	Pt ^c		164

^a MeCN/Et₄NClO₄; ^b MeCN/LiClO₄; ^c MeCN/Bu₄NBF₄.

in 83% and 50% yields, respectively. When the supporting electrolyte is replaced by Bu₄NBF₄, Me₂PhSiF is formed in a yield of 90%, presumably *via* exchange reaction between the chlorosilane formed initially and BF₄[−] (*cf.* Refs 27, 35, 71, and 105).

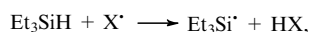
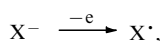
Electrooxidation of hydrosilanes in DME/Bu₄NBF₄ in an undivided cell with Pt electrodes affords polysilanes in overall yields of 32%–70%.



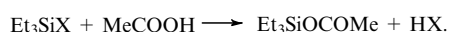
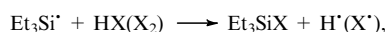
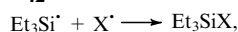
R = Ph, *n*-C₆H₁₃, *n* = 2–6.

The oxidation potentials of hydrosilanes¹⁶⁴ are 200 mV smaller than that of the polymer; this prevents the latter from oxidation with rupture of the polysilane chain according to a scheme similar to that described by Diaz *et al.*^{165, 166}

The electrically catalysed anodic substitution of hydrogen in the molecule of hydrosilane **42** by an acetoxy-group,¹⁶⁷ like processes of direct anodic substitution, occurs without oxidation of the nucleophile (CH₃COOH), the transferring agent being generated from the electrolytic additive (I[−], Cl[−], NO₃[−]). The transferring agent reacts with the hydrosilane **42** by a radical mechanism and at potentials smaller than the potential of oxidation of the acetate anion.



42

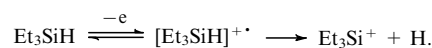


X = I, NO₃, ClO₄.

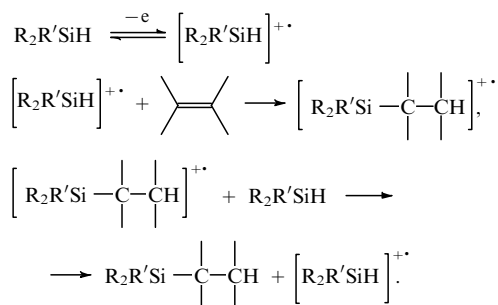
The same process catalysed by bromide ions by a redox mechanism and carried out using (C₁₀H₂₁)₄NBr or Et₄NBr as supporting electrolytes and EtOH or PrOH as nucleophiles yields triethylalkoxysilanes in 30%–95% yields.¹⁶⁸

Radical cations resulting from electrooxidation of silanes R₃SiH have been identified as adducts with tetracyanoethylene.¹⁶⁹ The lifetime of the radical cation derived from the silane **42** and detected using a rotating disc-ring electrode is equal to 0.003–

0.006 s.^{161, 163} In the absence of radical traps, this radical cation decomposes with the abstraction of a hydrogen atom.



In the presence of cyclohexene, the radical cation [**42**]^{+\cdot} adds to the double bond.^{162, 163, 170} The reaction occurs by a chain mechanism, the role of the anode being limited to its initiation (creation of the initial concentration of the radical cations in the solution equal to 10^{−10} M).



R = R' = EtO; R = Cl, R' = Me.

2. Di- and poly-silanes

The redox properties of polysilanes resemble those of carbon compounds with conjugated double bonds: the HOMO energy of polysilanes increases with increase in the number of linked silicon atoms (this increase is more pronounced than the decrease in the LUMO energy), which results in an increase in their electrochemical activity in oxidation reactions.

The potentials of oxidation of aliphatic disilanes (Table 7), like potentials E_p of other derivatives containing two identical or different elements of the silicon group, obey a linear correlation with vertical gas-phase ionisation potentials (IP) with a slope of less than unity. The latter has been attributed to the influence of the fast kinetics of decomposition of the radical cation and the solvent on E_p .¹⁷¹

In the series of diaryltetraalkyl-, arylpentamethyl- and hexaalkyldisilanes, both types of electron transfer during reduction have been found; stepwise electron transfer was observed in compounds in which a silicon atom carries at least one aromatic substituent and dissociative electron transfer was observed for aliphatic disilanes.¹⁷² An electron-withdrawing NO₂ group in the *para*-position of the aromatic ring destabilises the SOMO of the radical cation so markedly that in the case of bis(*p*-nitrophenyl)tetramethyldisilane, the type of electron transfer changes: the stepwise mechanism is replaced by dissociative mechanism, and the oxidation potential E_p is smaller than that calculated from the IP for reversible electron transfer.

The E_0 values calculated for hexamethyldisilane and Me(Si-Me₂)₃Me are approximately 1 V smaller than their effective potentials E_p , which is due to the high energy of reorganisation (38±5 kcal mol^{−1}) for these compounds.¹⁷⁴

Of the two peaks of oxidation of polysilanes of the composition [(MeSiFc)(MeSiPh)_n]_x, where *n* = 5, 7 and 25, with ferrocenyl (Fc) groups, the one corresponds to the process involving the Fc moiety (+ 0.4 V vs SCE), while the other (E_p = 1.15 V) is associated with the oxidation of the polysilane chain.¹⁶⁵

Polysilane films deposited on a platinum electrode exhibit an irreversible oxidation peak,¹⁶⁶ the potentials of which for alkylpolysilanes lie in the range 1.4–1.6 V (vs SCE) and depend only slightly on the nature of the alkyl substituent. Conversely, the potentials for arylpolysilanes depend appreciably on the electronic effects of the substituents in the aromatic ring, which is manifested in the anodic shift of E_p by 0.3–0.6 V (Table 7). This difference is caused by the marked increase in the relative HOMO

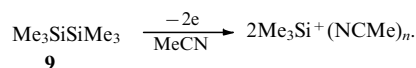
Table 7. Oxidation potentials of linear di- and poly-silanes.

Compound	E_p /V, vs SCE	$E_{1/2}$ /V (Ag/AgClO ₄ , GC electrode)	Ref.
Me ₃ SiSiMe ₃	1.76 ^a ($v = 0.1 \text{ V s}^{-1}$)		171
	1.880 ($v = 0.1 \text{ V s}^{-1}$)		173
	($E_0 = 0.92$) ^b		174
		1.48 ^c	69
	1.667		172
Pr ₃ SiSiPr ₃	1.542		172
BuMe ₂ SiSiMe ₂ Bu	1.563		172
Et ₃ SiSiEt ₃	1.76 ^a		171
<i>p</i> -MeOC ₆ H ₄ SiMe ₂ SiMe ₃		0.82	94
<i>p</i> -MeC ₆ H ₄ SiMe ₂ SiMe ₃		0.93	94
<i>p</i> -NCC ₆ H ₄ SiMe ₂ SiMe ₃	1.632		172
PhMe ₂ SiSiMe ₃		1.05	94
PhCH ₂ SiMe ₂ SiMe ₃		1.05	94
(<i>p</i> -MeOC ₆ H ₄ SiMe ₂) ₂	1.307		172
(<i>p</i> -NCC ₆ H ₄ SiMe ₂) ₂	1.616		172
(<i>p</i> -O ₂ NC ₆ H ₄ SiMe ₂) ₂	1.735		172
Me ₃ SiMe ₂ SiSiMe ₃	1.40 ^d ($v = 0.1 \text{ V s}^{-1}$)		171
	1.520		173
	($E_0 = 0.55$) ^b		174
Me(SiMe ₂) ₄ Me	1.330		173
Me(SiMe ₂) ₅ Me	1.180		173
Me(SiMe ₂) ₆ Me	1.075		173
[MePhSi] _{<i>n</i>}	1.0		166
[(<i>p</i> -MeOC ₆ H ₄)MeSi] _{<i>n</i>}	0.69		166
poly(methyl-β-phenethylsilane)	1.30		166
poly(cyclohexylmethylsilane)	1.42		166
[<i>n</i> -C ₆ H ₁₃ MeSi] _{<i>n</i>}	1.44		166
[(<i>n</i> -C ₆ H ₁₃) ₂ Si] _{<i>n</i>}	1.60		166
[Me ₂ Si] _{<i>n</i>}	1.0		166

^a vs. Ag/AgCl; MeCN/Et₄NClO₄, $E_{p/2} = 1.36 \text{ V}$ vs Fc/Fc⁺ (MeCN/-Bu₄NClO₄, Pt);¹⁷⁵ ^b the E_0 values calculated vs SCE are given in parentheses; ^c vs Ag/0.1 M AgNO₃; ^d vs Ag/AgCl; MeCN/Et₄NClO₄, $E_{p/2} = 1.10 \text{ V}$ vs Fc/Fc⁺ (MeCN/Bu₄NClO₄, Pt).¹⁷⁵

energy of the polysilane chain due to its interaction with the π orbitals of an aromatic substituent.

The E_p potentials for linear permethylpolysilanes decrease as the length of the chain increases and are related almost linearly to the ϵ_{HOMO} value calculated by the Sandorfi method.¹⁷³ A scheme including the formation of a silicenium adduct with acetonitrile ($n = 1$ or 2) has been proposed for the two-electron reduction of the disilane **9**.¹⁷³

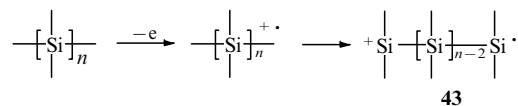


During reverse scanning, two peaks (-0.25 and -1.0 V vs SCE) were detected in the cathodic region; they were attributed to reduction of the adducts with different n .

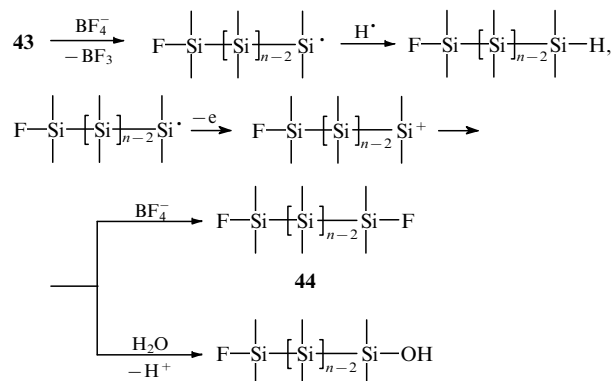
Cyclic polysilanes are oxidised in two steps ($E_p^1 = 1.1 - 1.4 \text{ V}$, $E_p^2 = 1.4 - 1.9 \text{ V}$ vs SCE).¹⁷⁶ The potential of the first step also depends on the number of silicon atoms linked to one another.¹⁷⁷ However, the character of this dependence is disturbed by another factor that determines the electrochemical reactivity, namely, by the magnitude of the Si–Si–Si angles, which varies as a function of the size of the ring. For cyclosilanes with $n = 3 - 7$, the E_p potential diminishes with a decrease in the size of the ring ($7 \approx 6 \approx 5 > 4 > 3$), because the ring becomes more strained. For cyclopolysilanes with $n > 9$ in which the strain of the ring is no longer significant, only a tendency of E_p to decrease, similar to

that observed in the series of linear polysilanes, was pointed out; however, the numerical values of the potentials were not reported.¹⁷⁶

Preparative oxidation of cyclopolysilanes is accompanied by ring opening yielding intermediate **43** in which the charge and spin densities are separated in space.^{176, 177}



When the process is carried out in the presence of Et₄NBF₄ in CH₂Cl₂/MeCN (4 : 1), α,ω -difluorinated products **44** are formed.¹⁷⁶



It was assumed that ring opening occurs *via* the formation of the intermediate radical cation,^{176, 177} although the variation of the E_p potentials in various solvents¹⁷⁷ (MeCN/CH₂Cl₂) indicates that this is rather an electrochemically irreversible process.

3. Disilenes

Sterically hindered disilenes are irreversibly oxidised in THF at a stationary platinum electrode at close potentials (Table 8), which indicates that the HOMO energy levels of these compounds are close to one another.¹⁵³ Since the interaction between the occupied π orbitals of the disilene and the aromatic fragments in tetraaryldisilenes is weak due to the substantial difference between their energies, the redox properties and the low oxidation potentials are determined by the π -electrons of the disilene bridge.

Table 8. Potentials of the oxidation peaks of disilenes R¹R²Si=SiR¹R² in THF/0.1 M Bu₄NPF₆ at a Pt electrode; $v = 0.2 \text{ V s}^{-1}$.

R ¹	R ²	E_p /V vs SCE
Mes	Mes	0.38
2,4-Me ₂ C ₆ H ₄	2,4-Me ₂ C ₆ H ₄	0.47
4-Bu ^t -2,6-Me ₂ C ₆ H ₃	4-Bu ^t -2,6-Me ₂ C ₆ H ₃	0.48
Mes	Bu ^t	0.54
Mes	1-Adamantyl	0.36

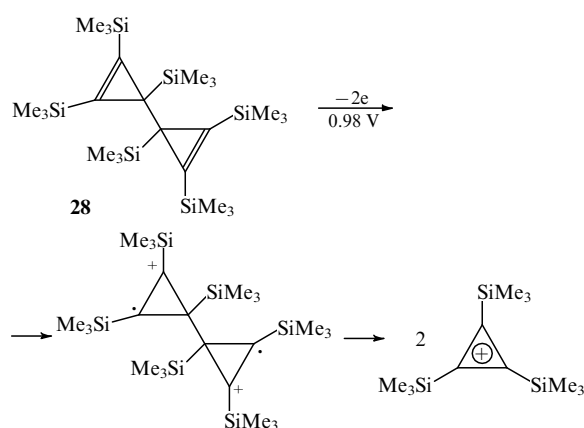
4. Tetraorganosilanes

The potential of oxidation of Et₄Si ($E_p = 2.56 \text{ V}$ vs SCE), like potentials of alkyl derivatives of metals (Ge, Sn, Pb, Hg) obey a linear correlation with the gas-phase IP.¹⁷⁸ Since the steric factors have no influence on the linear ratio of free energies, the process is assumed to occur as an outer-sphere electron transfer followed by a fast chemical reaction, the rate of which is higher than the rate of the transfer of an electron to the radical cation; this accounts for the fact that the process as a whole is chemically irreversible.

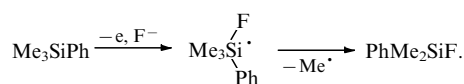
Electrooxidation of Ph₄Si ($E_{1/2} = 2.1 \text{ V}$ vs Ag/0.01 M Ag⁺), PhSiMe₃ and Ph₂Si(OH)₂ in CH₂Cl₂/AlCl₃ at a Pt electrode results in black polymeric precipitates being formed on the surface

of the electrode; these precipitates have been found to incorporate conjugated aromatic fragments.¹⁷⁹ When PhSiH_3 is oxidised at a rotating disc Pt electrode, an oxidation peak ($E_p = 2.1$ V) associated with the passivation of the electrode can be observed. Preparative electrolysis afforded a black polymer similar to that resulting from oxidation of the silane **46**, because disproportionation of the initial silane in the presence of AlCl_3 gives rise to the silane **46** and SiH_4 . Oxidation of 2-methyl-2-vinyltetraphenylcyclotrisiloxane gives the same conductive polymer as the oxidation of the silane **46**, since the latter is one of the oxidation products of this phenylcyclotrisiloxane.

Hexakis(trimethylsilyl)-3,3'-bicyclopropenyl **28** undergoes irreversible two-electron oxidation in $\text{MeCN}/(\text{C}_6\text{H}_{13})_4\text{NClO}_4$ being thus converted into a biradical dication, which decomposes to give two cyclopropenyl cations.¹⁸⁰



Oxidation of a number of tetraalkyl- and trialkylaryl-silanes at a controlled potential in the $\text{MeCN}/\text{Et}_4\text{NF} \cdot 3\text{HF}$ system at Pt electrodes results in the anodic substitution of fluorine for one of the alkyl groups in the silane (Table 9).¹⁸¹ In the presence of F^- anions, the oxidation potential of trimethylphenylsilane decreases by 300 mV (+2.6 and +2.3 vs $\text{Ag}/0.1$ M AgNO_3 with Et_4NClO_4 and $\text{Et}_4\text{NF} \cdot 3\text{HF}$, respectively), which is due to the F^- -assisted single-electron oxidation of the organosilane. After the formation of a Si–F bond, the intermediate radical with pentacoordinated silicon eliminates the most stable alkyl radical.



Alkyl radicals with $E_{1/2} > 2.3$ V ($\text{Me}^\cdot$) either dimerise or add an $\text{H}^\cdot$ atom, whereas the radicals with $E_{1/2} < 2.3$ V ($\text{Et}^\cdot$, $\text{PhCH}_2^\cdot$) are oxidised at the anode to give the corresponding carbocations.

Silanes with a Si–H bond can also be fluorinated by an electrochemical procedure;¹⁸¹ however, in the presence of $\text{Et}_4\text{NF} \cdot 3\text{HF}$, catalytic protodesilylation of R_3SiH to give R_3SiF occurs at a Pt electrode, in parallel with the electrochemical process.

Redox processes involving niobocene complexes with silicon-containing cyclopentadienyl rings and the EPR spectra of their cationic forms have been described.¹⁸²

Table 9. Anodic fluorination of organosilanes ($Q = 1.2$ F mol⁻¹).¹⁸¹

Tetraorgano-silane	Fluorosilane	Yield (%)	Products formed from $\text{R}^\cdot$
PhSiMe_3	PhSiMe_2F	80	CH_4 , C_2H_6
$p\text{-FC}_6\text{H}_4\text{SiMe}_3$	$p\text{-FC}_6\text{H}_4\text{SiMe}_2\text{F}$	80	CH_4 , C_2H_6
$\text{PhCH}_2\text{SiMe}_3$	Me_3SiF	50	PhCHO
$\text{PhCH}_2\text{SiEt}_3$	Et_3SiF	70	PhCHO
Et_3SiMe	$\text{MeSiEt}_2\text{F} + \text{Et}_3\text{SiF}$	45	EtF , $\text{CH}_2=\text{CH}_2$
		5	CH_4 , C_2H_6

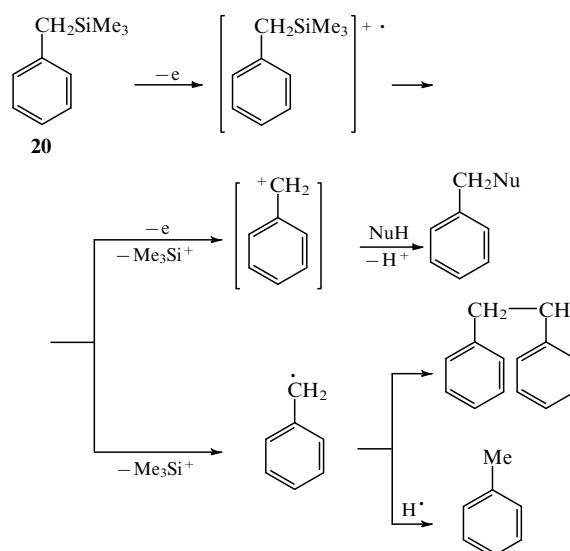
5. Allyl and benzylsilanes

A distinctive feature of compounds containing a silicon-containing substituent in the β -position with respect to the double bond is σ – π -conjugation between the bonding σ orbital of the Si–C bond and π -electrons of the double bond. As a consequence, the energy of the HOMO of the unsaturated fragment increases,^{183, 184} and, hence, the potentials of electrooxidation of these compounds are markedly lower than the oxidation potentials of compounds that do not contain this fragment (Table 10). Another consequence of the β -effect is that the Si atom in the radical cations derived from benzyl- and allylsilanes becomes more electrophilic. This facilitates cleavage of the C–Si bond (Me_3Si^+ is a ‘super-proton’) and the occurrence of nucleophilic reactions involving this centre.^{185–191}

The oxidation potentials of β -silyl-substituted unsaturated compounds obey a linear correlation with their first IP with a regression slope of less than unity.¹⁹⁵

In a study of oxidation of a series of benzyltrialkylsilanes substituted in the ring, it has been shown that in the case of $p\text{-MeOC}_6\text{H}_4\text{CH}_2\text{SiPr}_3$ and $p\text{-MeOC}_6\text{H}_4\text{CH}_2\text{SiMe}_3$, this process involves the formation of a radical cation that was detected by voltammetry.¹⁹¹ In a non-nucleophilic medium, the potential-determining reaction between the radical cations of benzylsilanes is first order (rupture of the C–Si bond). The reactivity of benzylsilanes is described by a three-parameter model that takes into account the polar effect of the substituent in the aromatic ring and also the inductive and steric effects of the alkyl groups at the Si atom. The relative sensitivity of the potential-determining reaction (ρ_c) to the inductive effect of alkyl substituents is higher than the sensitivity of E_0 (ρ_π), and this accounts for the apparent opposite influence of the +I effect of alkyl groups on the effective potential E_p ($\rho_I < 0$).

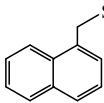
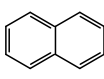
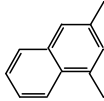
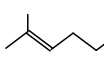
Oxidation of trimethylsilylmethanes with π -electron substituents (benzyl, allyl) in the presence of alcohols, carboxylic acids¹⁸⁹ or water¹⁸⁷ results in the formation of anodic substitution products incorporating C–O bonds. It is assumed that initially, the benzyltrimethylsilyl radical cation is formed; subsequently, it loses the Me_3Si^+ fragment and the resulting radical is oxidised to a benzyl cation.



When the process is carried out at a glassy carbon electrode (which is favourable for the adsorption of aromatic fragments) in the presence of Et_4NOTs (the surface activity of TsO^- is lower than that of ClO_4^-), dibenzyl and toluene resulting from transformations of the benzyl radical are also formed.

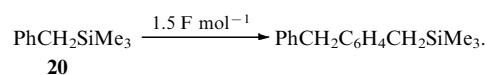
In the absence of additional nucleophiles in the solution, an unoxidised benzyltrimethylsilane molecule can act as a nucleophile. For example, oxidation of benzyltrimethylsilane **20** in the

Table 10. Potentials of electrooxidation of β -silyl-substituted π -systems.

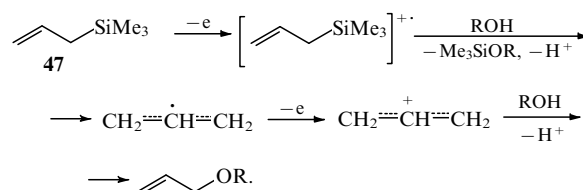
Compound	E_p /V (vs SCE, $v = 0.1 \text{ V s}^{-1}$)	$E_{1/2}$ /V (vs Ag/Ag ⁺)	Ref.
PhCH ₂ SiMe ₃	1.38 ^a 1.84 ^b		189, 192 186
		1.48 1.22 ^c 1.40 ^c	188 193 194
	1.627		191
<i>p</i> -MeC ₆ H ₄ CH ₂ SiMe ₃	1.17 ^{a, b} 1.56		189, 192 191
<i>o</i> -MeC ₆ H ₄ CH ₂ SiMe ₃	1.18 ^a		192
<i>p</i> -ClC ₆ H ₄ CH ₂ SiMe ₃	1.66		191
<i>m</i> -Me ₃ SiCH ₂ C ₆ H ₄ CH ₂ SiMe ₃	1.60 1.12 ^a		195 192
		1.14 ^d	196
<i>p</i> -Me ₃ SiCH ₂ C ₆ H ₄ CH ₂ SiMe ₃	1.06 ^a		192
		0.96 ^d	196
<i>o</i> -Me ₃ SiCH ₂ C ₆ H ₄ CH ₂ SiMe ₃	1.13 ^a		192
		1.08 ^d	196
<i>p</i> -MeOC ₆ H ₄ CH ₂ SiMe ₃	1.20 ^a 1.34		192 191
<i>m</i> -MeOC ₆ H ₄ CH ₂ SiMe ₃	1.55		191
<i>o</i> -MeOC ₆ H ₄ CH ₂ SiMe ₃	1.37 ^a		192
<i>p</i> -MeC ₆ H ₄ CH ₂ SiEt ₃	1.58		191
<i>p</i> -MeOC ₆ H ₄ CH ₂ SiPr ₃	1.40		191
PhC(SiMe ₃) ₃	1.70		195
<i>p</i> -(Me ₃ Si) ₃ CC ₆ H ₄ C(SiMe ₃) ₃	1.36		195
(Me ₃ SiCH ₂) ₂ C=C(CH ₂ SiMe ₃) ₂	0.87		195
<i>p</i> -MeOC ₆ H ₄ C(O)SiMe ₃	1.84 ^c		141
<i>p</i> -Bu ^t C ₆ H ₄ C(O)SiMe ₃	1.90 ^c		141
<i>m</i> -MeC ₆ H ₄ C(O)SiMe ₃	1.75 ^c		141
PhC(O)SiMe ₃	1.88 ^c		141
<i>m</i> -CF ₃ OC ₆ H ₄ C(O)SiMe ₃	2.10 ^c		141
<i>p</i> -CF ₃ OC ₆ H ₄ C(O)SiMe ₃	2.20 ^c		141
PhC(O)SiPhMe ₂	2.02 ^c		141
CH ₂ =CHCH ₂ SiMe ₃		1.58 1.70 ^{d, c}	193 197
CH ₂ =CMeCH ₂ SiMe ₃		1.28	193
Me ₂ C=CHCH ₂ SiMe ₃		0.92	193
PhCH=CHCH ₂ SiMe ₃		0.91 ^d	185
		0.96 ^d	185
		0.96 ^d	185
		0.94 ^d	185
	1.3 ^{b, c}		187

^a Referred to sat. Ag/AgNO₃, MeCN/Bu₄NBF₄, Pt; ^b the v value was not given; ^c calculated from IP₁ vs Ag/Ag⁺; ^d $E_{p/2}$ /V is given; ^e vs Ag/AgCl.

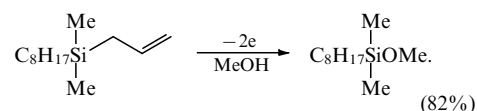
CH₂Cl₂/Bu₄NClO₄ in a divided cell at a Pt anode gives benzyl-(trimethylsilylmethyl)benzene in 30% yield.¹⁸⁹



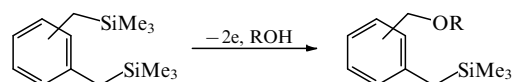
Oxidation of allylsilanes, in particular, allyltrimethylsilane **47**, also involves the intermediate formation of a cation, which reacts with a molecule of an O-nucleophile giving the final product.¹⁸⁷



The regioselectivity of the formation of products, which does not depend on the nature of the nucleophile but is governed by the substituents at the double bond is evidence supporting the above mechanism. In the only study¹⁸⁷ where the subsequent transformations of the silyl fragment have been followed, it has been shown that alkoxytriorganosilane is formed as the final product.



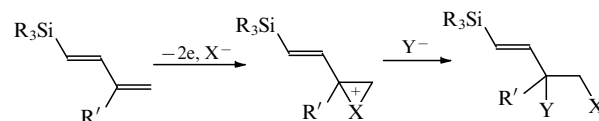
When α, α' -bis(trimethylsilyl)xylenes are oxidised in the presence of alcohols, only one Me₃Si fragment undergoes anodic substitution.¹⁹² No α, α' -dialkoxylated xylenes or products of alkoxylation of the ring are formed. This selectivity of the reaction is due to the fact that the remaining Me₃Si group stabilises the cationic intermediate, and the oxidation potential of the mono-alkoxylated product is more positive than that of the initial bis(trimethylsilyl)xylene.



The abstraction of a trimethylsilyl fragment leads to a cation, in which the positive charge is localised on the benzylic carbon atom and does not migrate to the β -position of the ring. This is confirmed by the fact that the reaction products contain no *p*- or *o*-quinodimethanes.¹⁹²

6. 1-Trialkylsilyl-1,3-alkadienes

Oxidation of 1-trialkylsilyl-1,3-alkadienes in solutions of alkali metal chlorides or bromides in water-organic media¹⁹⁸ yields only kinetically and thermodynamically controlled 3,4-adducts.



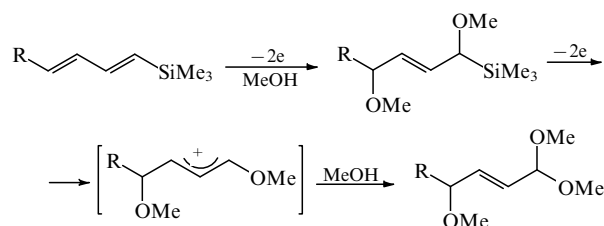
R = Me, Et; R' = H, Me; X = Cl, Br;

Y = Cl, Br, OH, OMe, OEt, OAc.

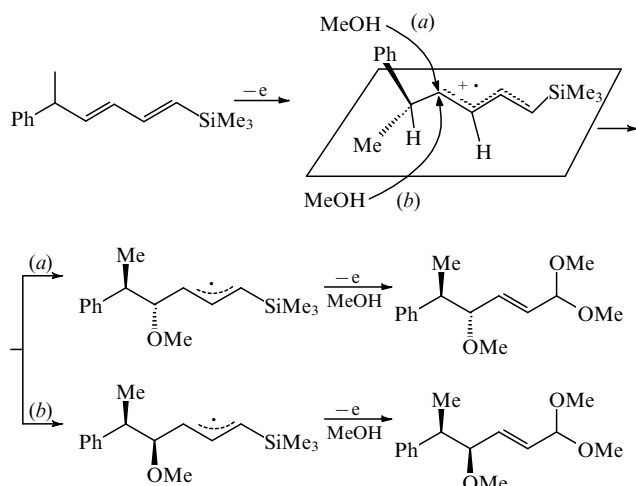
The authors cited explained the high regioselectivity of electrochemical halogenation by the occurrence of single-electron reduction of the unsaturated molecule to give a radical cation, the spin density of which, as shown by extended Hückel quantum-chemical calculations, is mostly localised on the terminal carbon atom of the conjugated system. However, according to the Markovnikov rule, regioselectivity of this addition should apparently be governed by the possibility of resonance stabilisation of the cationic intermediate rather than by the spin density.

Oxidation of 1-trimethylsilyl-1,3-dienes in methanol¹⁹⁹ at a carbon electrode gives rise to α, β -unsaturated 1,1,4-trimethoxy-

alkenes (29%–76%). The latter are readily hydrolysed with dilute HCl to the corresponding α,β -unsaturated aldehydes.



The overall process requires ~ 4.2 F of electricity per mole of the diene; the first half of the electricity passed is consumed in the formation of the silylated allylic intermediate, while the rest of the electricity is spent for its further oxidation, similarly to the process described in another study.¹⁸⁷ Only *trans*-products are formed. The diastereoselectivity of the oxidative methoxylation of 5-phenyl-1-trimethylsilyl-1,3-hexadiene is due to the fact that methanol preferably attacks the radical cation from its less sterically hindered side.¹⁹⁹ The overall yield of the stereomers is 53%.

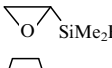
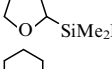
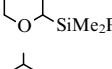
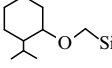
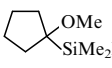
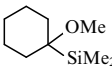
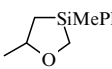
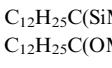
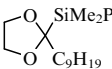
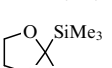
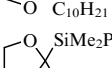
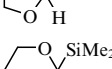
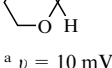
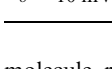


7. β -silyl ethers

The main characteristic feature of compounds containing silicon in the β -position with respect to the heteroatom (O, S, N), so that its p orbitals can be involved in conjugation with a π -system (if it is present in the molecule), is that the σ_{C-Si} bonding orbital interacts fairly strongly with the lone electron pair of the heteroatom. Although this effect depends on the nature of the heteroatom and on the mutual arrangement of the interacting orbitals, it usually markedly increases the HOMO energy of the molecule and thus facilitates its electrooxidation (E_{ox} decreases by 200–800 mV). Owing to this effect, the silicon atom becomes more electrophilic, especially after the transfer of an electron; as a result, nucleophilic reactions at this site occur at high rates.

Quantum-chemical calculations of HOMO energies as functions of the Si–C–O–C torsional angle have shown²⁰⁰ that when this angle is equal to 0° (a configuration with perpendicular arrangement of the C–Si bond with respect to the p orbital of oxygen), the HOMO level is relatively low and mostly corresponds to the σ orbital. The energy of the HOMO increases as the torsional angle increases and reaches its maximum at an angle of $\sim 95^\circ$. In this configuration, the C–Si bond and the oxygen p orbital are nearly parallel and can overlap efficiently with each other. The maximum destabilisation of the HOMO by the silicon atom in this configuration is 0.9 eV. The results of quantum-chemical calculations are in full agreement with the character of variation of the oxidation potentials (E_p) of alkoxy-silanes in which rotation around the C–O bond is hindered and the dihedral angle has a fixed magnitude (cyclic silicon-containing ethers in Table 11). The introduction of one more silyl group in the

Table 11. Oxidation potentials (vs Ag/AgCl) of acylsilanes and alkoxy-silanes.

Compound	E_p / V	$E_{1/2}$ / V	Ref.
$C_{10}H_{21}C(O)SiMe_3$	1.45		201
$C_9H_{19}C(O)SiMe_3$		1.62	202
$C_9H_{19}C(O)SiPhMe_2$		1.37 ^a	203
$C_9H_{19}C(O)SiPh_2Me$		1.38 ^a	203
$C_9H_{19}C(O)SiPh_3$		1.40 ^a	203
$C_8H_{17}CH(OMe)SiMe_3$	1.6	1.46 ^a	203
$MeOCH_2SiMe_3$	1.9		201
$MeOCH(SiMe_3)_2$		1.85	202, 204
$Me_3SiCH_2O(CH_2)_2OCH_2SiMe_3$		1.54	202, 204
$C_7H_{15}CH(SiPhMe_2)OMe$	1.60 ^b	~ 1.9	204
$C_7H_{15}CH(SiMe_3)OMe$	1.72 ^b		205
$C_7H_{15}CH(SiPhMe_2)OSiMe_2Bu^t$	1.95 ^b		205
$C_7H_{15}CH(SiPhMe_2)OH$	1.70 ^b		205
$C_8H_{17}CH(SiPhMe_2)OH$	1.70		205
$HOC_6H_4OCH_2SiMe_3$		1.07 ^c	206
$MeOC_6H_4OCH_2SiMe_3$		1.20 ^c	206
$NCC_6H_4OCH_2SiMe_3$		1.02 ^c	206
$O_2NC_6H_4OCH_2SiMe_3$		2.06 ^c	206
$ClO_2SC_6H_4OCH_2SiMe_3$		2.14 ^c	206
 $SiMe_3Ph$	2.15 ^b		205
 $SiMe_2Ph$		1.84	200
 $SiMe_2Ph$	1.67 ^b		205
 $SiMe_2Ph$		1.53	200
 $SiMe_2Ph$	2.08 ^b		205
 $SiMe_2Ph$		1.70	200
 $SiMe_2Ph$		1.83	202, 204
 $SiMe_2Ph$	1.63	1.50	200
 $SiMe_2Ph$	1.45	1.38	200
 $SiMe_2Ph$	1.82		200
$C_{12}H_{25}C(SiMe_3)_2OMe$	1.48		200
$C_{12}H_{25}C(OMe)_2SiMe_3$	1.50		200
 $SiMe_2Ph$	1.47	1.27	200
 $SiMe_3$	1.45	1.36	200
 $SiMe_2Ph$	1.50	1.55	200
 $SiMe_2Ph$	2.0		200

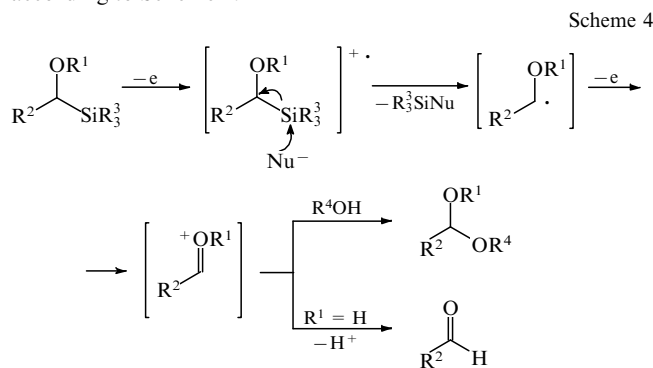
^a $v = 10 \text{ mV s}^{-1}$; ^b $v = 50 \text{ mV s}^{-1}$; ^c vs SCE.

molecule results in further decrease in E_p indicating that the HOMO level becomes even higher. An additional oxygen-containing substituent also decreases the oxidation potential (presumably, owing to an increase in the statistical weight of conformers that are favourable for electron transfer) (Table 11).²⁰⁰

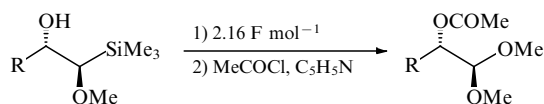
Anodic processes involving β -silyl ethers are accompanied, as a rule, by oxidative rupture of the $C_\alpha-Si$ bond and by the addition

of the nucleophile present in the solution to the resulting carbocation.

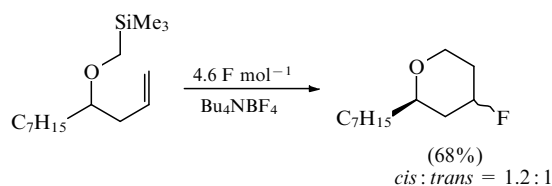
Oxidation of alkoxyasilanes has been assumed²⁰⁵ to occur according to Scheme 4.



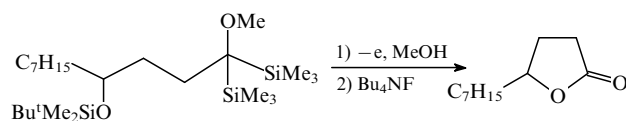
This process was used as one of the stages in the iteration synthesis of optically active polyols.²⁰⁶



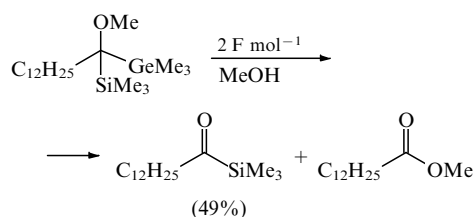
Electrooxidation of unsaturated α -silyl-substituted ethers results in the formation of a new C–C bond with the closure of a ring.²⁰⁷ This process conducted in the presence of PF_6^- or BF_4^- gives rise to cyclic fluorinated *cis*- and *trans*-derivatives.



A β -gem-disilane methoxymethyl group acts as a sort of 'latent carboxyl', which can be activated by electrooxidation.²⁰⁸ For example, oxidation of gem-disilane containing a protected (as a *tert*-butyldimethylsilyl ether) hydroxyl group is accompanied by cyclisation. This reaction has been used at the final stage of the synthesis of γ -undecalactone.^{208–210}



Oxidation of alkoxyasilanes containing a trimethylgermyl group, which is more easily eliminated as a carbocation, makes it possible to prepare acylsilanes.²⁰² Tridecanoyltrimethylsilane is formed (yield 49%) together with some methyl tridecanoate; the latter results from oxidation of the acylsilane itself under galvanostatic conditions and is formed in 96% yield when 5 F mol⁻¹ of electricity is passed through the solution.



8. β -Silyl sulfides

The electronic effects acting in the molecules of ethers are also typical of the molecules of β -silyl sulfides, but in the latter case, they are markedly weaker, because the 3*p* energy level of the S

Table 12. Oxidation potentials of β -silyl sulfides and thiophenes.

Compound	E_p/V^a (vs Ag/AgCl)	Ref.
PhSCH ₂ SiMe ₃	1.10 (1.15)	200 194
MeSCH(Ph)SiMe ₃	0.99 ^b	189
C ₈ H ₁₇ CH(SPh)SiMe ₃	1.10 1.25	200 210
C ₈ H ₁₇ C(SPh) ₂ SiMe ₃	1.20	200
C ₈ H ₁₇ C(SiMe ₃) ₂ SPh	1.10	200
RHSiMe ₃ ^c	0.99 ^d	211
RBu ^t SiMe ₃ ^c	0.95 ^d	211
RPhSiMe ₃ ^c	0.85 ^d	211
R(SiMe ₃) ₂ ^c	0.70 ^d	211
R(SnMe ₃)SiMe ₃ ^c	0.44 ^d	211
	1.92 ^e	212
	1.14 ^e	212
	1.92 ^e	212
	0.85 ^e	212
	2.05 ^e	216

^a $E_{1/2}$ vs SCE are given in parentheses; ^b vs Ag/AgNO₃ (sat.);

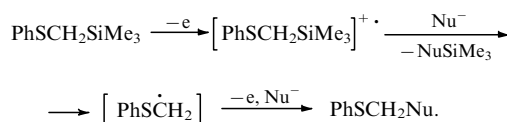
^c R = ; ^d vs. Ag/0.1 M AgNO₃; ^e vs SCE.

atom is much higher than those of the orbitals forming the C–Si bond, and these orbitals cannot interact as efficiently as those in the molecules of the oxygen analogues. Reactions involving β -silyl sulfides are similar to the corresponding reactions of β -silyl ethers and are determined by the ease of elimination of the trimethylsilyl group as a cation during anodic substitution.

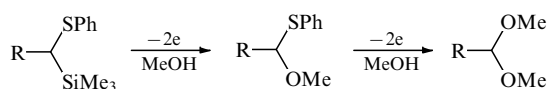
The oxidation potentials of β -silyl-substituted sulfides are somewhat lower than those of unsaturated compounds. The introduction of additional organylthio- or trimethylsilyl groups does not cause further decrease in E_p (Table 12).

Alkoxylation and acetoxylation of β -silyl phenyl sulfides occurs during their anodic oxidation in the presence of alcohols and carboxylic acids (Scheme 5).^{189,197,207} The yields of the reaction products vary depending on the nature of the nucleophile (25%–66%).

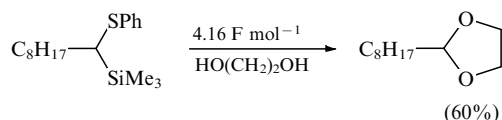
Scheme 5



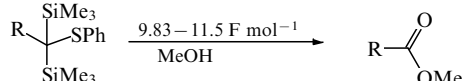
1-Phenylthio-1-trimethylsilylalkanes are oxidised in the presence of monohydric alcohols (overall, 4 F mol⁻¹ of electricity is required) to give the corresponding acetals in high yields (64%–84%).²¹⁰ The process includes two stages. Initially, 1-methoxy-1-phenylthioalkane is formed (2 F mol⁻¹); it can be detected during the reaction by chromatography or isolated from the reaction mixture. The subsequent two-electron oxidation of this compound is accompanied by rupture of the C–S bond and affords acetals.



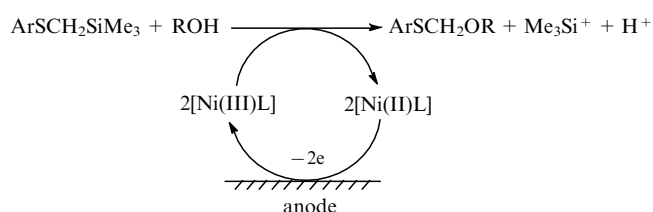
Conduct of the process in the presence of dihydric alcohols makes it possible to synthesise cyclic acetals.²¹⁰



Upon electrooxidation in MeOH, 1-phenylthio-1,1-bis(trimethylsilyl)alkanes are converted into the corresponding methyl carboxylates.²⁰⁹

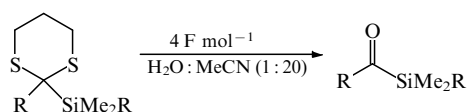


Alkoxylation of β -trimethylsilyl aryl sulfides, similar to the process shown in Scheme 5, has been accomplished using homogeneous redox catalysis by a cyclam complex of Ni(III).²¹³



Ar = *p*-Tol, Ph; L is cyclam.

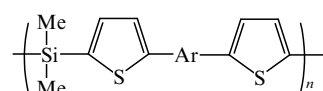
A trimethylsilyl group present at the 2-position of 1,3-dithianes somewhat decreases the potential of their irreversible oxidation but to a lesser extent than an alkyl group (Table 12).²¹¹ The relatively weak effect of the β -Me₃Si group is due to its equatorial position. When two trimethylsilyl groups are attached to the C(2) atom in 1,3-dithianes, the orientation of one of them becomes favourable for interaction of its $\sigma_{\text{C-Si}}$ orbital with the 3*p* orbital of the S atom, which facilitates oxidation of the dithiane. This effect is even more pronounced for a Me₃Sn substituent, because the energy of $\sigma_{\text{C-Sn}}$ bond is closer to that of the 3*p* orbital of the S atom. Oxidation of 2-trialkylsilyl-1,3-dithianes does not involve the C–Si bond; the yields of the corresponding acylsilanes are 70%–96%.²¹⁴ If the substituent R contains an unsaturated fragment, the reaction affords α,β -unsaturated acylsilanes.



R = Me, Bu^t.

In the oxidation of aryl trimethylsilylmethyl selenides,^{121,217} the β -effect of the Me₃Si group changes in principle the character of the potential-determining reaction of the electrically generated radical cations ($\text{E} + \text{C}_{\text{DIM}} + \text{Cl}$ instead of $\text{E} + \text{Cl} + \text{E}$ as for aryl alkyl selenides), despite the fact that this effect is the least pronounced in the series of β -silylated isostructural compounds of Group VIA elements ($\Delta E_{1/2} \cong 50 \text{ mV}$). Oxidation of aryl trimethylsilylmethyl selenides and sulfides in a non-nucleophilic medium²¹⁷ is accompanied by rupture of the Se–C_{sp³} and S–C_{sp³} bonds rather than the Si–C_{sp³} bond (*cf.* Refs 189, 197, 207 and 210).

The voltammetric behaviour of α,α' -silyl-²¹² and β -silyl-substituted polythiophenes,²¹⁵ polythiophenes based on tetrathienylsilane (C₄H₃S)₄Si,²¹⁶ polymers with units

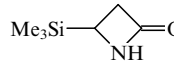


(where Ar are mono- or polynuclear substituted aromatic fragments)²¹⁸ and polymers prepared from 2,5-bis(trimethylsilyl)-thiophene, bis(2-thienyl)dimethylsilane, 1,2-bis(2-thienyl)tetramethyldisilane and bis(2-thienyl)diphenylsilane²¹⁹ have been reported. Electropolymerisation of silyl-substituted thiophenes, like polymerisation of unsubstituted thiophene, has been carried out by galvanostatic oxidation of the monomers in solution in nitrobenzene.^{212, 215, 216, 219}

9. β -Silylamines and carbamates

Based on the voltammetric behaviour of silylated cyclic amines derived from pyrrolidine, piperidine and perhydroazepine,²²⁰ ($n = 1$; $i/v^{1/2} = \text{const}$, the absence of reversibility of the oxidation peak at the sweep rate $v = 1 \text{ Vs}^{-1}$ at -35°C), it has been suggested that a low-stability radical cation is formed. Substituents at the Si atom, the size of the ring and the presence of methyl groups have only a slight influence on E_p (Table 13), whereas in

Table 13. Oxidation potentials of silyl-substituted amines (vs SCE).

Compound	E_p/V	$E_p/2/\text{V}$	Ref.
PhNHCH ₂ SiMe ₃		0.44 ^a	194
Ph ₂ NCH ₂ SiMe ₃		0.41 ^a	194
PhNHCH ₂ SiMe ₂ Ph		0.45 ^a	194
PhNHCH ₂ SiMeBu ₂		0.48 ^a	194
PhNHCH ₂ SiMe ₂ (C ₈ H ₁₇)		0.48 ^a	194
<i>p</i> -MeOC ₆ H ₄ NHCH ₂ SiMe ₃		0.26 ^a	194
Ph ₂ N(CH ₂) ₂ SiMe ₃		0.74 ^a	194
PhNH(CH ₂) ₂ SiMe ₃		0.60 ^a	194
Ph ₂ N(CH ₂) ₃ SiMe ₃		0.75 ^a	194
Me(Me ₃ SiO) ₂ SiCH ₂ NC ₄ H ₈	0.56		220
Me(Me ₃ SiO) ₂ SiCH ₂ NC ₆ H ₁₂	0.50		220
Me(Me ₃ SiO) ₂ Si(CH ₂) ₂ NC ₄ H ₈	0.77		220
Me(Me ₃ SiO) ₂ Si(CH ₂) ₃ NC ₆ H ₁₂	0.72		220
Me ₃ SiR ^b	1.00		220
Me ₃ SiCH ₂ NC ₅ H ₁₀	0.65		220
Me ₃ SiCH ₂ R ^b	0.62		220
Me ₃ Si(CH ₂) ₂ R ^b	0.90		220
Me ₃ Si(CH ₂) ₂ R ^c	0.90		220
Me ₃ Si(CH ₂) ₃ R ^b	0.90		220
Me ₃ Si(CH ₂) ₃ R ^c	0.90		220
Me ₃ SiNC ₄ H ₄	1.35		221
Me ₃ SiNC ₅ H ₁₀	1.00		220
Me ₃ SiN(CH ₂) ₄ CH ₂ OH	1.173 ^d		221
PhNHSiMe ₃		0.73 ^d	194
Et ₃ SiNEt ₂		1.23	222
Me ₂ (NC ₅ H ₁₀)SiC $\equiv$ CH		1.29	222
MeVin(NC ₅ H ₁₀)SiC $\equiv$ CH		1.00	222
Me ₂ Si(NEt ₂) ₂		1.35	222
MeVinSi(NEt ₂) ₂		1.08	222
MeSi(NEt ₂) ₃		1.12	222
VinSi(NEt ₂) ₃		0.98	222
Ph(CH ₂) ₂ N(CO ₂ Me)CH ₂ SiMe ₃	1.45		200, 223
Me ₃ Si- 	1.75 ^c		224
Silatranes	1.4–1.8		225

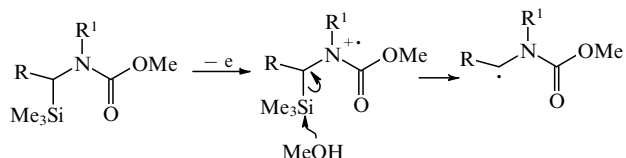
^a $v = 20 \text{ mVs}^{-1}$; ^b R = ; ^c R = ; ^d E_0 ; ^e vs Ag/AgCl.

the presence of a CH₂ fragment between the Si and N atoms, the E_p value becomes 1.3–1.4 V lower than those for compounds containing no silyl substituent.

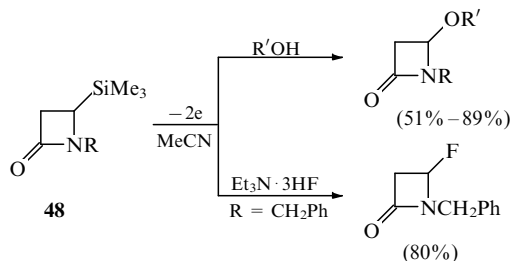
This type of variation of the potentials, which is also typical of aromatic *N*-(trimethylsilylmethyl)amines,¹⁹⁴ is associated with the resonance interaction between the trimethylsilylmethyl group and the cationic centre of the radical cation induced by the charge transfer. This interaction is enhanced on passing from the initial compound to the transition state.

The decrease in the potentials of oxidation of nitrogen-containing compounds following the introduction of a β -trimethylsilyl group is relatively small for amines and is more significant for carbamates.²⁰⁰ This manifestation of the β -effect is due to the fact that conjugation with the carbonyl group decreases the energy of the p orbital of the nitrogen atom in the molecules of carbamates and thus facilitates its more efficient overlap with the bonding σ_{C-Si} orbital.

Preparative processes involving this type of compound are similar to those involving β -silyl ethers and sulfides. They include anodic substitution of an appropriate nucleophile for the trimethylsilyl group. The carbamates activated by a silyl group undergo electrooxidation with cleavage of the C–Si bond and regioselective methoxylation of the α -carbon atom.²²³ The corresponding α -methoxycarbamates are obtained in yields of 68%–100%.



N-Substituted 4-trimethylsilylazetidin-2-ones **48** are also converted into alkoxylation and acyloxylation products. When Et₃N·3HF is added to the solution of an electrolyte, fluorinated products of anodic substitution are formed.²²⁴

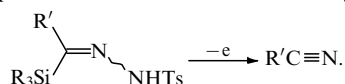


R = H, PhCH₂;

R' = Ac, Me, CH₂CHMe₂, CH₂CH=CH₂, (CH₂)₂CH=CH₂, PhCH₂.

Oxidation of [(*N*-methylbenzylamino)methyl]trimethylsilane in the presence of MeOH or EtOH is the only example of reaction in which the C–Si bond in a β -silyl-substituted nitrogen-containing compound does not undergo oxidative rupture but, instead, the C–N bond is cleaved.¹⁸⁹ This leads to bis(benzylmethylamino)methane rather than to alkoxylation products.

Electrooxidation of tosylhydrazones of acylsilanes in an undivided cell affords the corresponding nitriles.²⁰³ The process requires 3.2–4.4 F mol^{−1} of electricity.



In a divided cell, the formation of nitriles requires a catalytic amount of electricity ($Q = 0.26$ – 0.8 F mol^{−1}); the yields of nitriles are markedly higher.

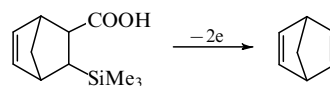
10. β -Silyl-substituted derivatives of carboxylic acids

Anodic oxidation of β -trimethylsilyl-substituted carboxylic acids affords only terminal alkenes as the final products, because at the carbocation stage resulting from oxidative decarboxylation of the

initial molecule, the process is controlled by the trimethylsilyl group.²²⁶

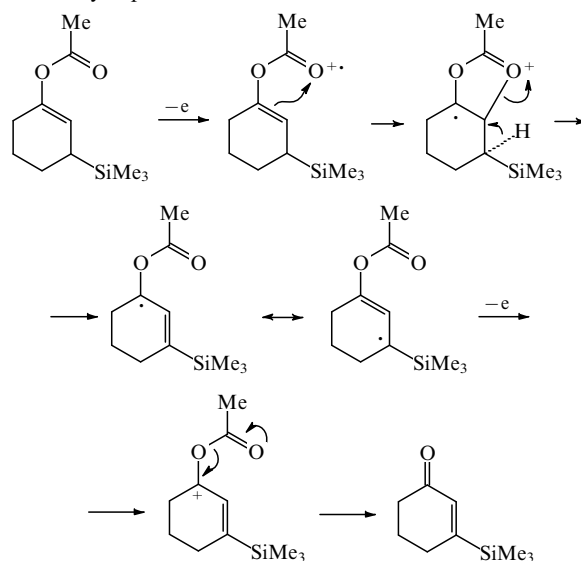


Oxidative decarboxylation–desilylation has been used in the synthesis of 2,5-norbornadiene.¹⁵⁸



11. β -Silyl-substituted enol acetates

Oxidation of β -silyl-substituted enol acetates yielding α,β -unsaturated β -silylcycloalkenones is the only known reaction in which the trimethylsilyl group does not undergo oxidative elimination from the allylic position.²²⁷



The process is believed to include cyclisation of the primary radical cation, which is converted by deprotonation into an α -radical stabilised by the silicon atom. This effect, together with the antiparallel arrangement of the C $_{\beta}$ –H bond with respect to the C–O⁺ bond being cleaved in the oxonium intermediate, results in the rupture of the C $_{\beta}$ –H bond instead of the C $_{\beta}$ –Si bond which is cleaved in the case of allyl- and benzyl-silanes.

12. Siloxy-derivatives

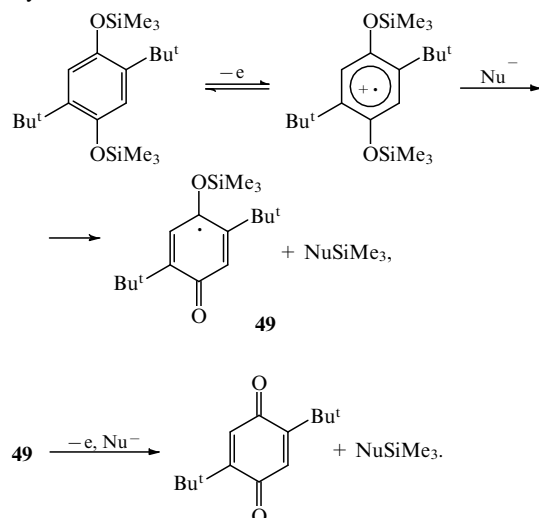
The oxidation potentials of trialkylsiloxybenzenes are virtually determined by the first siloxy-group attached to the aromatic ring. The introduction of the second group of this type changes E_p only slightly²²⁸ (Table 14).

Table 14. Oxidation potentials of trialkylsiloxybenzenes R¹R²R³R⁴C₆H₂ in MeCN/0.1 M LiClO₄ (Pt electrode, $v = 0.1$ V s^{−1}).

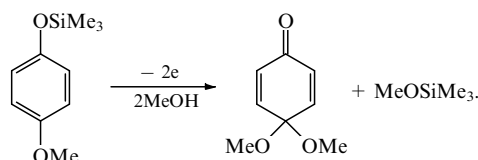
R ¹	R ²	R ³	R ⁴	E_p /V (vs SCE)
1-Me ₃ SiO	4-Me ₃ SiO	H	H	1.10
1-Me ₃ SiO	4-Me ₃ SiO	2-Cl	H	1.25
1-Me ₃ SiO	4-Me ₃ SiO	2-Bu ^t	5-Bu ^t	1.05
1-Bu ^t Me ₂ SiO	4-Bu ^t Me ₂ SiO	2-Bu ^t	5-Bu ^t	1.07
1-Me ₃ SiO	4-Me ₃ SiO	2-MeO	H	1.05
1-Me ₃ SiO	4-MeO	H	H	1.14
9-Me ₃ SiO ^a	10-Me ₃ SiO	H	H	0.78

^a 9,10-Bis(trimethylsiloxy)anthracene.

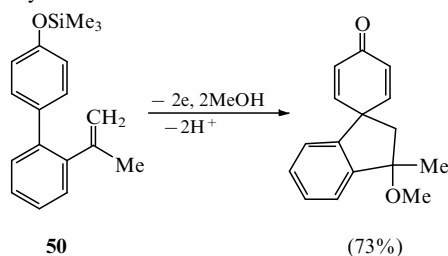
Trimethylsilyl ethers of hydroquinone lose Me_3Si fragments during oxidation and, *via* the intermediate formation of radicals **49**, they are converted into the corresponding quinones in 65%–92% yields.²²⁸



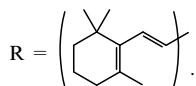
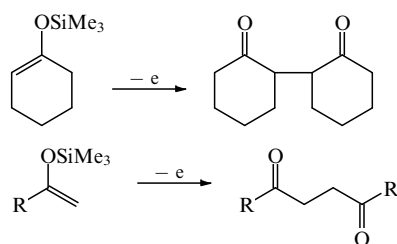
Under similar conditions, monosilylated 4-methoxy-1-(trimethylsiloxy)benzene gives rise to 4,4-dimethoxy-2,5-cyclohexadienone (yield 99%).²²⁸



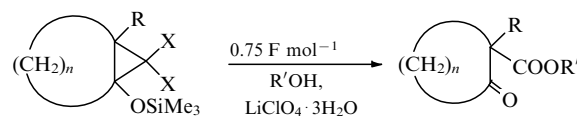
Anodic oxidation of the trimethylsilyl ether of 4-(2'-alkenyl)phenol **50** carried out in MeOH (Pt anode, 0–10 °C) is accompanied by the elimination of the trimethylsilyl group and by intramolecular cyclisation involving the double bond of the alkenyl substituent.²²⁹



Silyl ethers of enols undergo electrooxidation to give γ -diketones. The latter result from dimerisation of either the primary radical cations or the radicals arising after the oxidative rupture of the Si–O bond.²³⁰

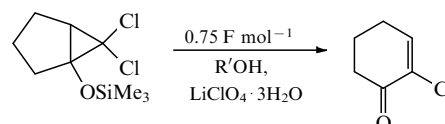


β -Oxoesters are formed in the electrooxidation of 1-trimethylsilyloxybicyclo[*n*.1.0]alkanes²³¹ in ethanol in the presence of $\text{Fe}(\text{NO}_3)_3$ in a divided cell at a Pt electrode.



$n = 4, 5, 10$; $R = \text{H, Me}$; $X = \text{H, Br, Cl}$.

Under the same conditions, 6,6-dichloro-1-trimethylsilyloxybicyclo[3.1.0]hexane yields only the product of ring expansion.



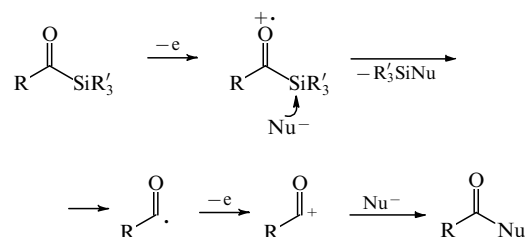
It was noted that the maximum yield of β -oxoesters is observed at –13 to –10 °C, but neither the reason for this effect nor the role of $\text{Fe}(\text{III})$ were discussed.

13. α -Silyl esters

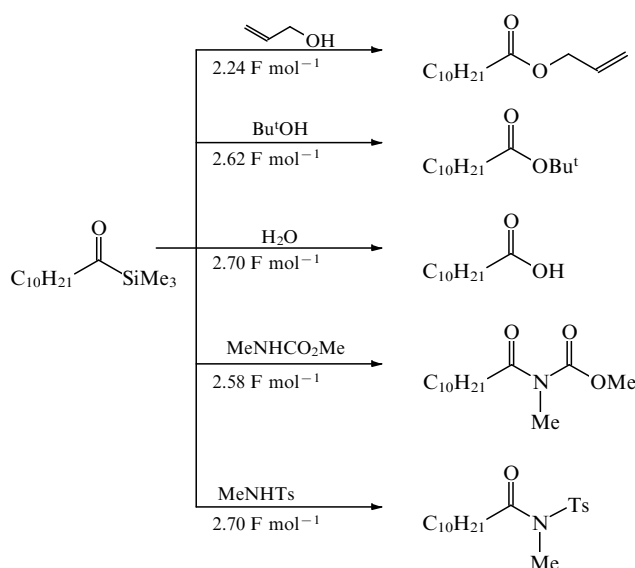
The oxidation potentials of acylsilanes in which the silicon atom is attached to an electron-withdrawing carboxylic group are smaller than the potentials of the corresponding alkoxyasilanes (see Table 11).^{201, 203} In terms of the concept of $\sigma_{\text{C-Si}}-\rho_{\text{O}}$ conjugation, this is explained by the rigid fixing of the orbitals in the carbonyl compound, which ensures their efficient overlap, and by the possibility of free rotation around the C–O bond in alkoxyasilanes, which results in a lower probability of efficient conjugation in the latter case. However, in the case of adiabatic stepwise transfer of an electron during oxidation (which assumes that a primary radical cation is present on the reaction coordinate), stabilisation of the radical cation by the β -effect of the silyl group should be identical for these two types of compound (owing to the free rotation). Therefore, the experimental observation in question is rather associated with the fact that the C=O bond is shorter than C–O. This ensures more efficient overlap of the interacting orbitals, which destabilises the HOMO of the initial molecule and thus decreases the oxidation potential of acylsilanes.

Preparative oxidation of acylsilanes, like the oxidation of allyl- and benzylsilanes, involves rupture of the C–Si bond and affords products of electrophilic reactions of the carbocationic intermediate.^{201, 203, 232} It has been assumed that the carbocation is formed *via* nucleophilic attack on the primary radical cation derived from acylsilane (Scheme 6).

Scheme 6



Electrooxidation of acylsilanes in the presence of a 5–6-fold excess of a nucleophilic reagent gives the corresponding products of anodic substitution in 69%–92% yields.²¹⁰

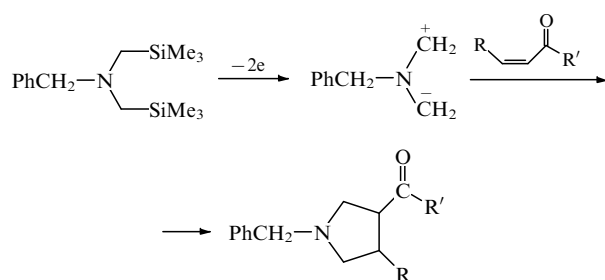


14. α -Silylamines

The appearance of the silyl group at the nitrogen atom in aniline (see Table 13) increases E_{ox} with respect to that of the unsubstituted compound, which is in agreement with the electron-withdrawing properties of the α - Me_3Si group.¹⁹⁴

The single-electron reduction of silylamines at a Pt electrode has been considered.²²² In the case of alkyl derivatives, the inductive mechanism of the transfer of electron density predominates, whereas, in the case of vinyl derivatives, the EPR data for the electrically generated radical cation $[\text{MeVinSi}(\text{NEt}_2)_2]^{\cdot+}$ made it possible to conclude that the positive charge and spin density are delocalised in the $\text{N}-\text{Si}-\text{N}$ group. However, in the latter case, there is no conjugation over the $\text{C}=\text{C}-\text{Si}-\text{N}$ system of bonds. The $\epsilon_{\text{HOMO}} - E_{\text{p}/2}$ plots for alkyl- and vinyl-substituted silylamines are separate straight lines for each family of compounds, which is due to the differences in the transfer of electronic effects.

Electrooxidation of bis(trimethylsilylmethyl)benzylamine in DMF is a convenient method for generation of 1,3-dipoles, which react with activated alkenes.²³³ The yields of the cycloaddition products vary in the range 8%–61% depending on the nature of the substituent in the alkene molecule.



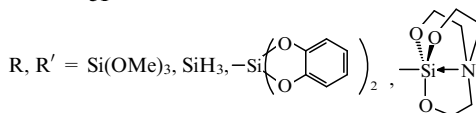
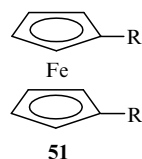
$\text{R} = \text{H}, \text{CO}_2\text{Me}, \text{Ph}; \text{R}' = \text{OMe}, \text{OBu}^t, \text{H}.$

The use of AcONa or KF as a supporting electrolyte is significant for efficient cycloaddition.

15. Compounds of hypervalent silicon

Comparison of the oxidation potentials of mono- and bis-pentacoordinated systems with silatrane ($E_{1/2} = -0.07$ and $+0.21 \text{ V vs SCE}$) or silylcatecholate fragments ($E_{1/2} = +0.07$ and $+0.31 \text{ V vs SCE}$) with the oxidation potentials of 1,1'-bis-silyl-substituted ferrocene derivatives **51** ($E_{1/2} = +0.55 \text{ V}$)²³⁴ has demonstrated an interesting electronic effect: a substantial decrease in the $E_{1/2}$ potential for the reversible $\text{Fe(II)}/\text{Fe(III)}$ pair is observed in the case of anionic and pentacoordinated compounds, whereas in the case of bis(trimethoxysilyl)ferrocene, a slight increase in this

potential has been found [$\Delta E_{1/2}$ for bis(trimethoxysilyl)ferrocene with respect to unsaturated ferrocene is $+0.09 \text{ V}$].

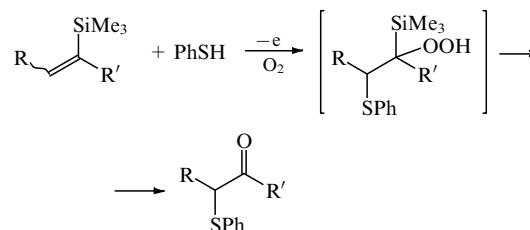


Thus, the coordination number proves to be an important factor determining the electronic properties of organosilicon compounds: tetracoordinated compounds exhibit electron-withdrawing properties, whereas pentacoordinated compounds are characterised by electron-donating properties (irrespective of their geometry). Although this effect has not yet received a clear explanation, it is assumed that the electron density in pentacoordinated organosilicon compounds is delocalised over the surrounding ligands. In this case, silicon acts as a donor of electrons and thus becomes more electrophilic. In the molecules of silatranes, the electron density is markedly displaced from nitrogen to iron through the silicon atom, owing to the bis-apical arrangement of these atoms in the trigonal bipyramid.

Voltammetric curves for R-silatranes ($\text{R} = \text{Me}, \text{Et}, \text{Vin}, \text{Ph}$) ($\nu = 0.2\text{--}0.5 \text{ V s}^{-1}$) are practically reversible, and the oxidation potential depends appreciably on the nature of R , which indicates that the $\text{N} \rightarrow \text{Si}$ interactions are retained during the electrode process.²²⁵

VII. Electrochemical processes involving organic derivatives of silicon

Electrooxidation of alkenylsilanes in the presence of PhSH and with molecular oxygen being bubbled through the solution requires a catalytic amount of electricity ($Q = 0.16$ to 1.19 F mol^{-1}) and is a direct and regiospecific pathway to α -phenylthio-substituted carbonyl compounds.²³⁵ The yields of the products depend appreciably on the nature of the substituents R and R' .



R	R'	Yield (%)
C_6H_{13}	H	12
H	C_8H_{17}	73
H	$\text{C}_8\text{H}_{17}\text{CH}(\text{OH})\text{CH}_2$	93
C_4H_9	C_4H_9	13

Oxidation ($Q = 0.04\text{--}3.77 \text{ F mol}^{-1}$) of 0.5 mmoles of 1-phenylthio-1-(trimethylsilyl)alkenes in the presence of 2–6 equivalents of thiophenol results in the formation of a product with two phenylthio-groups ($\text{R}' = \text{SPh}$) in a yield of 60%–99%.

During the electrochemically initiated oxygenation of 1-phenylthio-1-(trimethylsilyl)alkenes, only the $\text{C}-\text{Si}$ bond undergoes oxidative rupture, the $\text{C}-\text{S}$ bond remaining intact. A chain radical mechanism for this process has been proposed; this mechanism includes radical addition of the phenylthio radical to the double bond, reaction of the resulting C-radical with oxygen and abstraction of an $\text{H}^{\cdot}$ atom from PhSH by a peroxy radical, which yields hydroperoxide and regenerates the phenylthio radical.

Tetraethylsilane **45** has been obtained both in cathodic and anodic processes as a result of the radical attack by ethyl radicals (electrically generated by oxidation of EtMgBr or reduction of EtBr) on a silicon atom of the electrodes.²⁴¹ When ethyl chloride or acrylonitrile is used in this process, no organosilicon compounds are formed.

Tetraethoxysilane is prepared by oxidation of EtOH in the presence of $(\text{NH}_2)_2\text{CO} \cdot \text{HCl} + (\text{NH}_2)_2\text{CO}$ or $\text{Et}_3\text{N} \cdot \text{HCl} + \text{Et}_3\text{N}$ at a ferrosilicon anode.^{3, 242–245} Depending on the supporting electrolyte and its concentration and on the current density, the yield of the reaction product ranges from 3.3% to 60% based on the dissolved ferrosilicon.²⁴⁴

VIII. Conclusion

The character of silyl substitution (α - or β -substitution) in aromatic or heteroatomic molecules changes their electrochemical reactivity according to the influence of the silyl group on the frontier orbitals. α -Substitution decreases the LUMO energy and facilitates reduction reactions, whereas β -substitution increases the HOMO energy and decreases the IP, which accounts for the easier anodic oxidation of these compounds.

Evidently, electroreduction of chlorosilanes involves the activation type of electron transfer (although the Si–Cl bond is very strong) giving rise to silyl radicals, which are reduced at the potential of formation to silyl anions. For this reason, cathodic processes involving chlorosilanes occur by an ionic mechanism.

The crucial factor determining the behaviour of organosilicon radical-cation intermediates in anodic reactions is that trialkylsilyl groups are eliminated extremely easily in the cationic form. Therefore, organosilicon derivatives are quite attractive for functionalisation of organic compounds in the reactions of anodic substitution.

The publications dealing with the electrochemistry of organosilicon compounds can be clearly divided into two groups. The first group includes theoretical studies in which the electrochemical method is used to obtain characteristics of FMOs and to study orbital interactions, whereas the second group comprises purely preparative studies (synthetic studies based on the electrochemical generation of active intermediates and electrochemical initiation of reactions in the bulk of a solution). The studies of the first group usually deal with potentials of reversible redox pairs (the ion-radical components of which are so stable that they exist in solution over long periods without entering in any reactions), while the studies of the second group occur normally under non-controlled conditions, and potentials are often not used at all to characterise the reactivities of compounds.

It is clear that these two lines of research do not exhaust the potentialities of organic electrochemistry and, therefore, it is quite reasonable to expect that new studies in this field will be published. In particular, one might expect that studies dealing with elementary steps of electrochemical processes, kinetics and thermodynamics of electron transfer and of accompanying chemical reactions will appear, because it is the mechanistic investigations that would create the scientific grounds for controlling the reactivity of intermediates (and, hence, the nature of the final products) as early as at the stage of charge transfer and potential-determining reactions.

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Methods of description of the polycondensation kinetics and the structures of the polymers formed

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Abstract. The modern mathematical methods which make it possible to describe the kinetics of the formation reactions and the structures of polymers formed via polycondensation are examined: direct differentiation of an infinite system of differential equations, statistical approaches, and the concept of bond blocks. The possibilities and limits of applicability of each method are demonstrated. The bibliography includes 83 references.

I. Introduction

The mathematical procedures for the analysis of the kinetics of chemical reactions, based on the Law of Mass Action,¹ have been well developed. It would appear that the entire problem should reduce to finding procedures for the solution of a more or less complex system of differential equations describing the variation of the concentrations of the reactants as a function of time. However, when the formation reactions of polymers are examined, a series of problems arise. The first of them is that the kinetics of polymerisation processes depend significantly on the state of the reaction medium, which frequently varies in the course of the reaction.² The inhomogeneity of the distribution of the reaction centres in the initial stage of three-dimensional radical polymerisation, leading to cyclisation and ultimately to a high degree of localisation of the process,^{3,4} the variation of the viscosity inducing the gel effect in the radical polymerisation of certain monomers,⁵ as well as the inhibition of the reaction as a result of the vitrification of the system^{2,6–9} may serve as examples. Finally, the system frequently undergoes phase decomposition in the course of the process,¹⁰ which results in a change of the spatial distribution of the concentrations of the reactants. These factors are extremely difficult to take into account within the framework of formal kinetics.

Another difficulty consists in the need to analyse and solve an infinite system of differential equations because in principle, there is a possibility of the formation of an infinite number of reaction products — macromolecules of different size and with different structures. The approaches to the solution of such a system of

equations have already been outlined by Flory¹¹ and were later developed in many studies and surveyed in monographs.^{3,12,13} However, recently a series of new problems arose, particularly in connection with the wide scale employment of numerical methods based on the application of modern computational techniques. The principle of these is how to attain the required accuracy of the numerical solution and how to control it.

The development of modern experimental methods has reached a level such that the calculations of certain average quantities (for example, the number-average and weight-average molecular masses) have already become inadequate; more detailed information about the structure of the polymer is required from the kinetic calculation. However, any experimental methods for the study of the structures of polymers are also subject to an intrinsic error, which in fact determines the required accuracy of the calculation.

Hitherto statistical computational methods have been applied in kinetic investigations, which is due both to their simplicity and to the possibility of obtaining with their aid detailed information about the structures of complex formations such as, for example, network polymers. However, investigators do not always estimate correctly the applicability of these methods to the description of specific kinetic systems.

Finally, a new approach has appeared recently to the analysis of the formation reactions and structures of polycondensation polymers, based on the concepts of bond blocks.

All these factors have led to the writing of the present review.

It has to be stipulated immediately that the review will deal solely with the polycondensation method of synthesis of polymers. The characteristic features of the formation of the chain — unit by unit or from any fragments — actually determine the choice of qualitatively different systems of differential equations.^{3,14,15} The solution and analysis of the system describing polycondensation processes are in fact the most complex. Problems of this class are solved with the aid of the Smoluchowski equation,¹⁶ which was first proposed for the description of coagulation processes.^{17,18}

II. Direct methods for the solution of the Smoluchowski equation

1. Polycondensation of polymers with isotypical functional groups

The Smoluchowski equation has the following general form:

$$\frac{dx_i}{dt} = -x_i \sum_j k(i,j)x_j + \frac{1}{2} \sum_{j=1}^{i-1} k(i-j,j)x_{i-j}x_j, \quad (1)$$

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where x_i is the concentration of the species (in the given instance, macromolecules) with size i ($i = 1, 2, 3, \dots$ is the number of units in the chain) and $k(i, j)$ is the rate constant for the reaction between species with sizes i and j .

This equation describes a process which in the simplest case can be expressed in the form



The Smoluchowski equation is suitable for the description of the kinetics of a wide variety of processes and numerous studies have therefore been devoted to its analysis (see, for example, Refs 16 and 19–25).

When applied to the reactions of polymer formation, Eqn (1) characterises polycondensation as a result of the interaction of isotypical functional groups with one another. The dependence of the kinetic constants on the dimensions of the macromolecules (subject to the condition that Flory's postulate¹¹ of the independence of the reactivity of functional groups on the size of the macromolecules carrying these groups is valid) is due to the fact that the number of functional groups f_i and the size of the macromolecules are directly interrelated (in the absence of intramolecular cyclisation reactions).

In the simplest case of the f -functional polycondensation, we have

$$f_i = (f-2)i + 2. \quad (3)$$

Hence it follows that the effective rate constant for the reaction between macromolecules having the i th and j th sizes is

$$k(i, j) = f_i f_j k, \quad (4)$$

where k is the rate constant for the reaction between the corresponding functional groups.

A thorough analysis of the approaches to the solution of the Smoluchowski equation has been carried out.¹⁶ In their assessment of the functional relations $k(i, j)$, the authors do not confine themselves to Eqn (4) and consider also other more general relations:

$$k(i, j) = A + B(i+j) + Cij, \quad (5)$$

where A , B , and C are parameters the magnitude of which depends on the type of the monomer. Processes during which the relation

$$k(i, j) = A i^n j^m \exp(-Bij),$$

holds preferentially have also been analysed¹⁹ using numerical methods for the solution of Eqn (1).

The general approach to the solution of Eqn (1) is¹³ that they are convoluted with the aid of an integral transformation by introducing the so called generating function $F(s, t)$:

$$F(s, t) = \sum_i x_i(t) s^i, \quad (6)$$

where s is a parameter and t the process time.

As can be seen from Eqn (6), when the function $F(s, t)$ is expanded in series in s , the concentrations of the i -mers assume the roles of the coefficients of the corresponding powers of s . On differentiating $F(s, t)$ with respect to s for $s \rightarrow 1$, we obtain the moments of the distribution of x_i with respect to i . Eqns (1) then assume the form of a partial differential equation:

$$\frac{\partial F(s, t)}{\partial t} = -s \frac{\partial F(s, t)}{\partial s} \frac{\partial F(1, t)}{\partial s} + \frac{1}{2} \left\{ \frac{\partial F(s, t)}{\partial s} \right\}^2, \quad (7)$$

which can be solved by the method of characteristics.²⁶

If it is assumed that the index i in the designation of the concentrations x_i characterises not the size of the macromolecule, expressed as the number of monomer units, but its functionality, then, firstly, the relation $k(i, j)$ becomes universal, namely $k(i, j)$ is proportional to the product ij , and, secondly, Eqn (7) becomes applicable to any polycondensation system with isotypical functional groups.

The solution of Eqn (7) leads to the following result (in a parametric form):

$$F(s, t) = \sum_i x_i(0) \chi^i - \frac{t \left\{ \sum_i i x_i(0) \chi^{i-1} \right\}^2}{2(1 + \Phi t)}, \quad (8)$$

$$s = \chi + \left(\chi - \frac{\sum_i i x_i(0) \chi^{i-1}}{\Phi} \right) \Phi t. \quad (9)$$

Here $x_i(0)$ is the initial concentration of molecules with i functional groups (this quantity characterises the distribution of the initial molecules with respect to the types of functionality), χ is a parameter, and Φ is the initial concentration of functional groups.

It has been shown²⁷ that the solution of Eqns (7) branches at a certain critical point t_c on the time scale. If $t \leq t_c$, then $\chi(s) = 1$ when $s = 1$. Starting from the time t_c Eqn (9) has two roots: $\chi_1(1) = 1$ and $\chi_2(1) < 1$. The critical point corresponds to the onset of gel formation, while the second root χ_2 (less than unity) characterises the sol fraction of the system. On differentiating Eqn (9) with respect to s , we obtain an expression for the critical time:

$$\begin{aligned} \frac{\partial \chi}{\partial s} &= \frac{1}{1 + \Phi t \left\{ 1 - \sum_i i(i-1)x_i(0)\chi^{i-2}/\Phi \right\}} = \\ &= \frac{1}{1 - \Phi t(\bar{f}_w - 2)}, \end{aligned} \quad (10)$$

i.e.

$$\Phi t_c = \frac{1}{\bar{f}_w - 2}, \quad (11)$$

and for the critical conversion we have

$$\alpha_c = \frac{\Phi t_c}{1 + \Phi t_c} = \frac{1}{\bar{f}_w - 1}, \quad (12)$$

where

$$\bar{f}_w = \frac{\sum_i i^2 x_{i0}}{\sum_i i x_{i0}}.$$

Here $\bar{f}_w$ is the weight-average functionality³ of the initial system.

The branching of the solution of Eqn (8) may be confirmed by a general consideration of the initial Eqn (7) without resorting to its solution.²⁸

Indeed, successive differentiation of Eqn (7) with respect to the parameter s leads to the appearance of a chain of equations for the distribution moments:

$$\frac{\partial F'(s)}{\partial t} = -F'(s)F'(1) + F''(s)[F'(s) - sF'(1)], \quad (13)$$

$$\frac{\partial F''(s)}{\partial t} = F''(s)[F''(s) - 2F'(1)] + F'''(s)[F'(s) - sF'(1)], \quad (14)$$

etc. The primes in the equations denote the corresponding derivatives (first, second, and third) with respect to s .

When $s = 1$, the expressions in square brackets in the second terms on the right-hand sides of the equations become zero. As a result of this, the chain of equations is closed and this makes it possible to find explicitly the time variation of the distribution moments $F'(1)$, $F''(1)$, etc. However, as can be seen from Eqn (10), at the critical point the highest distribution moments tend to infinity. Thus the second term on the right-hand sides of the equations becomes indeterminate, because it represents the product of zero and infinity. This indeterminacy must be resolved, as it implies the appearance of the possibility of a different solution.

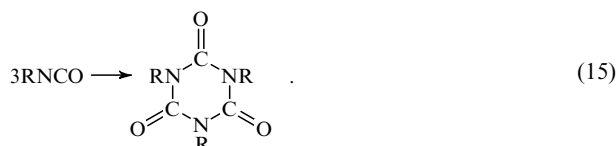
The size of the macromolecule and its functionality are unambiguously interrelated by a relation of type (3). However, in the general case, for an arbitrary initial distribution with respect

to functionality, it is not so easy to find the specific form of a relation of this kind. It is therefore reasonable, adopting the considerations put forward in a monograph,¹³ to introduce a two-index definition of the chains, where one of the indices characterises the size of the macromolecule and the other its functionality. If the polycondensation takes place as a result of the interaction of different functional groups, then a larger number of indices are introduced, each corresponding to a definite type of such functional groups. Thus it is possible to describe adequately a process occurring in an arbitrarily complex system.

2. Cyclotrimerisation

It is noteworthy that reactions with participation of only isotypical functional groups are encountered extremely rarely. One of the examples is the cyclotrimerisation of isocyanates^{29,30} and cyanic acid derivatives.³¹ Although these reactions can be formally regarded as polycondensation with participation of isotypical groups, a wide variety of aspects of which have been well investigated, the fact that the formation of a trifunctional unit takes place in one step must introduce certain characteristic features into the process kinetics. We shall discuss this problem.

The trimerisation process represents formally the simultaneous condensation of three functional groups, *i.e.* a termolecular reaction. For example, in the case of isocyanates, it can be described as follows:



However, the reaction mechanism is fairly complex.³² For example, the trimerisation of isocyanates takes place as a first-order reaction.^{33–35} It is of first order with respect to both the isocyanate groups and the catalyst and proceeds via a complex system of equilibria. In particular, the first stage is the formation of carbamates.³⁵ The time law governing the consumption of functional groups is determined by this factor. However, since the functional groups are distributed between different macromolecules, the probability of the reaction of each of them (the reaction rate) must be proportional to the product of the rate of reaction of the functional groups and the product of the concentrations of the corresponding macromolecules. Thus the differential equations describing the growth of macromolecules assumes form (1), but in terms of a certain fictitious time. We shall explain this in relation to a simple example.³⁶

Suppose that the functional groups Y are bound in a complex with a reagent Z:



where K is the equilibrium constant.

The rate of formation of the Y–Y bond as a result of, say, the interaction of species bound in a complex has been described by the expression

$$\frac{d[\text{YY}]}{dt} = k \left(\frac{Kz_0y}{1 + Ky} \right)^2, \quad (17)$$

where the symbols z and y designate the concentrations of the corresponding reactants and k is the reaction rate constant.

Evidently, depending on the product Ky , the reaction can be of both second and zero order with respect to the concentration of the functional groups y . However, if the formation reaction of the

dimer X_2 is described, then the multiplier x_1 appears in brackets in the numerator on the right-hand side of the equation whilst the denominator remains the same as before. Thus the kinetic equation for the formation of the dimer assumes the form

$$\frac{d[\text{X}_2]}{dt} = k \left(\frac{Kz_0y}{1 + Ky} \right)^2 x_1^2 = \frac{d[\text{YY}]}{dt} x_1^2, \quad (18)$$

or, after the introduction of the fictitious time,

$$\tau = \int \frac{d[\text{YY}]}{dt} dt, \quad (19)$$

$$\frac{d[\text{X}_2]}{dt} = kx_1^2. \quad (20)$$

A similar problem arises also in the case of reactions between an amine and an epoxide. The interaction of these reactants is also known^{37,38} to proceed via a complex system of donor–acceptor equilibria. The kinetic law governing the consumption of the epoxide groups should therefore be fairly complex.^{37–40} Thus the following kinetic equation has been proposed:⁴⁰

$$\frac{d\alpha}{dt} = k_1(1 - \alpha)^{n_1} + k_2\alpha^m(1 - \alpha)^{n_2},$$

where α is the degree of conversion with respect to the epoxide groups.

The simplest way of taking into account the complexity of the kinetic law consists in the use of an equation of type (19) in formulating the kinetic equations for the concentrations of macromolecules of different size, the consumption of the functional groups and the hydroxy- and epoxide groups (E) being disregarded.⁴¹ In this case

$$\tau = k[\text{OH}][\text{E}]_0^2 t.$$

Evidently, this approach may lead to significant errors. The system of donor–acceptor interactions, which determines the complexity of the process kinetics, varies over the course of the reaction³⁸ because not only the initial system components, the concentration of which falls as the process proceeds, but also the reaction products, the concentration of which increases, may participate directly in the equilibrium. Thus it would be more correct to express the fictitious time in an integral form, as in Eqn (19).

The question whether the complexity of the reaction mechanism may preclude the formulation of kinetic equations in the form of Eqn (1) was apparently first posed in the study of Stanford and Stepto⁴² in relation to the reaction of urethane formation. The problem was solved as follows: the application of Eqn (1) is possible if the degree of conversion is used instead of time as the independent variable. In essence, this claim agrees with Eqn (18). However, this conclusion has not been demonstrated rigorously and is more in the nature of an intuitive postulate.

When equations of type (1) are formulated for a cyclotrimerisation reaction, account is actually taken of its termolecularity,^{43,44} neglecting the complexity of the kinetic law.

Since the reaction products may contain only an odd number of oligomeric units and the chain length obeys the condition

$$i = 2n + 1, \quad (21)$$

whilst the number of functional groups in the macromolecule is defined by the relation

$$f_i = n + 2, \quad (22)$$

where n is the number of ternary knots arising as a result of cyclotrimerisation, an equation of type (1) can be written as follows:^{43,44}

$$\frac{dx_{2n+1}}{dt} = -(n+2)x_{2n+1} \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} (i+2)(j+2)x_{2i+1}x_{2j+1} + \frac{1}{3} \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} \sum_{k=0}^{\infty} (i+2)(j+2)(k+2)x_{2i+1}x_{2j+1}x_{2k+1} \quad (23)$$

$$i + j + k = n - 1.$$

Eqn (23) was solved by the method of generating functions.⁴³

If account is taken of the fact that the relation between the degree of polymerisation of the macromolecules i and the functionality is specified by the relation

$$f_i = \frac{i+3}{2}, \quad (24)$$

which follows from conditions (21) and (22), then the equation thus obtained assumes the form

$$\frac{\partial F(s, t)}{\partial t} = -\frac{1}{8} [sF'(s, t) + 3F(s, t)][(F'(1, t) + 3F(1, t))^2 + (sF'(s, t) + 3F(s, t))^3]. \quad (25)$$

It has been shown that the degree of critical conversion $\alpha_c = 0.5$, which agrees with experimental data.^{45–48}

An attempt has been made⁴⁴ to explain the experimentally observed⁴⁹ deviations of the observed value of α_c (0.60–0.66) by the decrease in the reactivity of the ‘suspended’ functional group compared with the initial reactivity, *i.e.* by the effect of substitution in the first sphere. A statistical approach was used as a method for the solution of the problem. The authors⁴⁴ found that, as the reactivity approaches zero, the degree of critical conversion tends to 0.66.

Several comments need to be made concerning the result obtained. Firstly, it has been shown^{32,33} that the reactivities of the initial and ‘suspended’ isocyanate groups are the same, *i.e.* that there is no substitution effect at least in the case of 1,6-hexamethylene diisocyanate. Secondly, as shown above, the gel formation point in the cyclotrimerisation of cyanate esters corresponds to 50% conversion.^{45–48} Finally, it has been established¹³ that the use of the statistical method of calculation in the presence of the substitution effect may lead to erroneous results. A striking confirmation of this conclusion has been obtained.⁵⁰

The kinetic effect of substitution in the first sphere implies that, when a polycondensation reaction, which in the simplest case can be represented by the scheme



is carried out, the kinetic constants are not equal to one another: $k_1 \neq k_2 \neq k_3$. As in Scheme (2), in Scheme (26) the index designates the number of monomer units in the macromolecule and f_i represents the functionality of the i -mer.

As shown in Fig. 1, the degrees of critical conversion calculated for the equilibrium polycondensation (where the results of the statistical calculation are applicable) and nonequilibrium polycondensation differ not only quantitatively but also qualitatively.

The cyclotrimerisation reaction is not of interest solely as a method of synthesis of a wide variety of thermally stable and heat-resistant polymers from a fairly wide class of monomers.³¹ The fact that three functional groups entering into the composition of three different macromolecules participate in the reaction introduces definite characteristic features also into the formal features

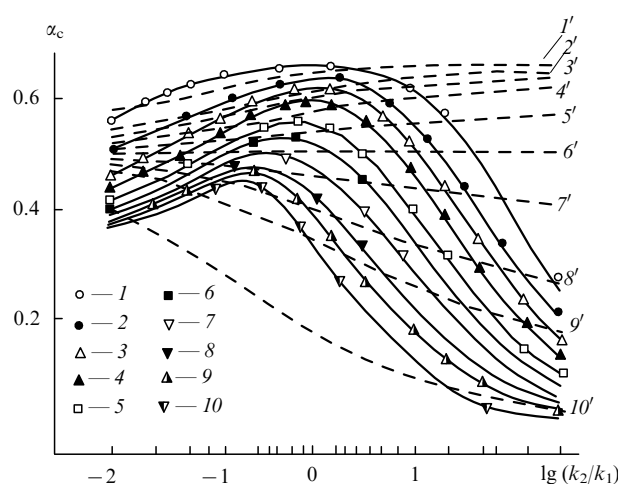


Figure 1. Dependence of the critical conversion (gel point) on the constant k_2/k_1 [see Scheme (26)] in irreversible (continuous lines) and equilibrium (dashed lines) 3-functional polycondensation.⁵⁰ The constants k_3/k_1 : (1) and (1') 0.01; (2) and (2') 0.05; (3) and (3') 0.1; (4) and (4') 0.2; (5) and (5') 0.5; (6) and (6') 1; (7) and (7') 2; (8) and (8') 5; (9) and (9') 10; (10) and (10') 100.

of the polycondensation. In particular, the solution of Eqn (25) by the method of characteristics affords the following result for the number-average degree of polymerisation $\bar{P}_n$ and the critical conversion α_c

$$\bar{P}_n = \frac{1}{1 - 2/3(\bar{f}_n \alpha)}, \quad (27)$$

$$\alpha_c = \frac{1}{2(\bar{f}_n - 1)}, \quad (28)$$

where

$$\bar{f}_n = \frac{\sum i x_{i0}}{\sum x_{i0}} \text{ is the number-average functionality.}^3$$

Evidently Eqns (27) and (28) differ from the classical equations, including Eqn (12), which characterises the critical conditions in f -functional polycondensation. This is why monofunctional monomers (for example, 1-chloro-6-hexamethylene isocyanate^{33,34}) do not terminate the network chain but play the role of a chain propagator, displacing the gel formation point towards higher conversions up to the formation of linear polymers. We shall carry out below a more thorough comparison of the cyclotrimerisation and 3-functional polycondensation processes on the basis of statistical analysis. Despite all the differences, these processes lead to the formation of 3-functional knots.

3. Polycondensation of monomers with heterotypical functional groups

The reaction between functional groups of different types (epoxide + amine, isocyanate + hydroxyl, hydroxyl + carboxyl, *etc.*) is a more common instance of polycondensation processes. If the polycondensation takes place as a result of the interaction of heterotypical functional groups and reaction between isotypical groups is impossible, then Eqn (7) is replaced by the expression

$$\frac{\partial F(\bar{s})}{\partial t} = -s_1 \frac{\partial F(\bar{s})}{\partial s_1} \frac{\partial F(\bar{1})}{\partial s_2} - s_2 \frac{\partial F(\bar{1})}{\partial s_1} \frac{\partial F(\bar{s})}{\partial s_2} + \frac{\partial F(\bar{s})}{\partial s_1} \frac{\partial F(\bar{s})}{\partial s_2}, \quad (29)$$

in which $\bar{s}$ is a vector, consisting in the given instance of two components, s_1 and s_2 , which refer to functional groups of two types.

The solution of the above equation by the method of characteristics leads to the following result, which has also been obtained in a parametric form:

$$F(\bar{s}, t) = \sum_i (x_{ai}\chi_1^i + x_{bi}\chi_2^i) - a\alpha_a, \quad (30)$$

$$a\alpha_a = b\alpha_b, \quad (31)$$

$$s_1 = \frac{\chi_1 - \alpha_a \sum_i i x_{bi} \chi_2^{i-1} / b}{1 - \alpha_a}, \quad (32)$$

$$s_2 = \frac{\chi_2 - \alpha_b \sum_i i x_{ai} \chi_1^{i-1} / a}{1 - \alpha_b}, \quad (33)$$

$$\alpha_a = b \frac{e^{(b-a)t} - 1}{be^{(b-a)t} - a}, \quad (34)$$

$$\alpha_b = a \frac{e^{(b-a)t} - 1}{be^{(b-a)t} - a}, \quad (35)$$

where x_{ai} and x_{bi} are the initial concentrations of the reactants carrying i functional groups of types A and B respectively (the initial distribution with respect to types of functionality), α_a and α_b are the degrees of conversion of groups A and B respectively, a and b are their initial concentrations, and χ_1 and χ_2 are parameters.

Differentiation of Eqns (32) and (33) with respect to s_1 and s_2 makes it possible to find the critical conditions:

$$\frac{\partial \chi_1(\bar{1})}{\partial s_1} = \frac{1 - \alpha_a}{1 - \alpha_a \alpha_b (\bar{f}_{wa} - 1)(\bar{f}_{wb} - 1)}, \quad (36)$$

i.e.

$$(\alpha_a \alpha_b)_c = \frac{1}{(\bar{f}_{wa} - 1)(\bar{f}_{wb} - 1)}, \quad (37)$$

where $\bar{f}_{wa}$ and $\bar{f}_{wb}$ are the weight-average functionalities with respect to groups A and B respectively.

4. Certain general comments

An analytical solution of Eqn (1) with the aid of generating functions can be found in rare instances. A kinetically complex system of equations with a large set of kinetic constants is usually susceptible only to a numerical solution. A convenient method involves the creation of a system of equations for the distribution moments. The system can be characterised experimentally by the first three moments (more precisely, the number-average and weight-average molecular masses and the yield of the polymer). In order to find these parameters in the case of the polycondensation of monomers with isotypical functional groups, a system of three equations has to be solved. Additional equations for mixed second moments appear in copolymerisation. Thus the system of equations increases to 10 components. Modern computational techniques makes it possible to readily solve problems of this kind (see, for example, Dzhevadyan *et al.*⁵¹).

However, the applicability of the method of moments is extremely limited. In particular, the equation for the moments cannot be obtained when Flory's principle of the independence of the constants of the size of the macromolecule does not hold or when the system is such that intramolecular cyclisation cannot be neglected. In the latter case, it is impossible to convolute Eqn (1) with the aid of the method of generating functions because an additional term arises in the equation, the dependence of which on the index has a fractional exponent.^{3, 12, 52} The system of equations (1) therefore has to be solved numerically. Complexities due to the incompleteness of the system then arise. Indeed, the first term on the right-hand side of Eqn (1) contains an infinite sum, which represents the overall concentration of the functional groups. In the absence of cyclisation, this quantity can be easily found by solving Eqn (13) with $s = 1$. However, as already stated above, an equation of type (13) cannot be obtained in the presence of the additional term taking cyclisation into account. Therefore the

system of Eqns (1) has to be solved directly and, since it is incomplete, the problem of the termination of infinite series of equations arises.

In the case of a direct solution of the system of equations, the only reasonable approach involves the estimation of the results of the calculation as a function of the number of equations solved. When the latter increases, the accuracy of the calculation should also increase. The attainment of the instant when the result obtained ceases to depend on the number of equations implies the possibility of terminating the chain of equations.

Examples of this approach to the solution of the problem of linear polycondensation when cyclisation reactions take place may be found in a number of communications.⁵²⁻⁵⁴

In the analysis of the results of their investigation, Irzhak *et al.*⁵² observed an interesting phenomenon — the attainment of a limiting yield of cyclic products (Fig. 2). Physically this effect is due to the fact that the rate of cyclisation is lower the longer the chain. Consequently, with increase in the degree of conversion and in the size of the macromolecules, the rate of cyclisation diminishes to a greater extent than the decrease in the rate of polycondensation as a consequence of the exhaustion of functional groups.

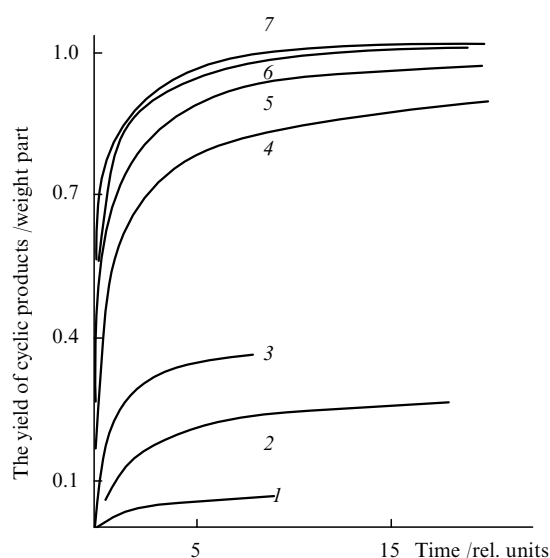


Figure 2. Kinetic curves for the accumulation of cyclic condensation products.⁵² Cyclisation constant k : (1) 0.1; (2) 0.5; (3) 1.0; (4) 5.0; (5) 10.0; (6) 20.0; (7) 50.0.

Another example refers to the determination of the conditions for the appearance of a nonmonotonic molecular mass distribution (MMD).

Direct calculation of the concentration of chains^{55, 56} made it possible to find a criterial relation between the kinetic constants of Scheme (26), which determines the nature of the MMD for a linear polymer. It has been observed⁵⁷⁻⁶⁰ that in certain cases a polymer with a nonmonotonic 'saw tooth' MMD is formed (Fig. 3). Analysis showed^{55, 56} that this is possible for a definite ratio of the kinetic constants. The condition

$$\frac{k_2^2}{k_1 k_3} \leq \frac{2}{3}, \quad (38)$$

is necessary, while the condition

$$\frac{k_2^2}{k_1 k_3} \leq \frac{\sqrt{2} - 1}{2}. \quad (39)$$

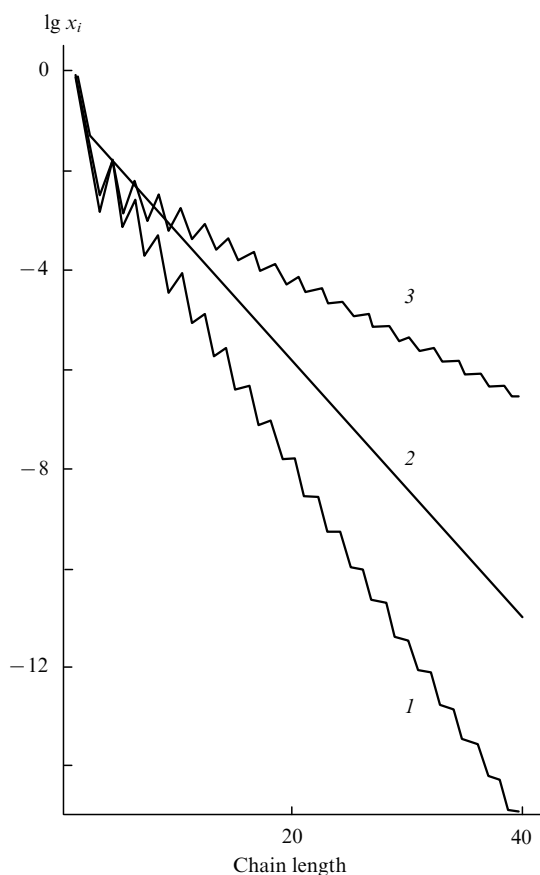


Figure 3. Numerical MMD function for a linear homopolymer⁵⁵ with the kinetic constants of Scheme (26); k_2/k_1 : (1) 0.1; (2) 3.0; (3) 0.4; k_3/k_1 : (1) and (2) 9; (3) 100. Degree of conversion 0.2.

is necessary and sufficient. As shown in Fig. 4, the above relations make it possible to separate the regions of existence of monotonic (region I) and nonmonotonic (region II) MMD.

Physically the nonmonotonic nature of MMD is due to the decisive role of the dimerisation rate constant. In this case, the formation of polymers with an even number of units is somewhat preferred. If a copolycondensation method is applied, then polymers with heterotypical end groups accumulate preferentially.

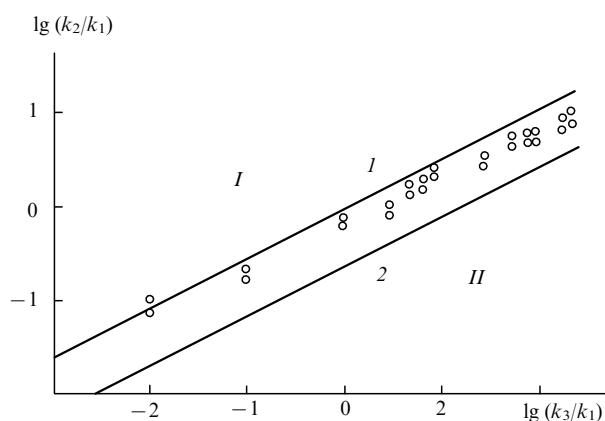


Figure 4. Regions corresponding to the existence of the monotonic (I) and nonmonotonic (II) MMD defined by the kinetic constants. Line I corresponds to Eqn (38) and line 2 to Eqn (39). The points in the transition region were obtained by direct calculation.

As early as 1942, Zel'dovich proposed a qualitatively different method for the analysis of an infinite system of differential equations.⁶¹ Its essential feature is that the particle growth process is regarded as random movement in the phase space of their sizes and is described by a partial differential equation. This idea was expressed in a more concrete form in other studies.^{24,25}

In formulating partial differential equations, it is assumed that the parameter Δi is the elementary step in the size space — it is small for a small particle size, *i.e.* for the first members of the series the system of differential equations must nevertheless be regarded as discrete. In this case, the question of the number of the equation from which one should go over to a continuous system and replace the sum by an integral assumes the main importance. In the analysis of a specific kinetic scheme, it has been shown²⁵ that the transition from a discrete series to a continuous equation was impossible up to numbers 50–100. Since the result obtained was expressed in the form of a certain function of particle size, the proposed approach made it possible to establish the distribution function also in the region of large sizes, which cannot be achieved in the numerical solution of a limited number of equations (1).

In conclusion of this section, we emphasise that the subdivision of the formation reactions of polymers in terms of a kinetic feature into polymerisation and polycondensation is extremely arbitrary. Indeed, even in radical polymerisation with formation of linear polymers, chain termination may occur as a result of the recombination of radicals. This implies that, together with the unit-by-unit addition (chain propagation reaction), the chain is formed also as a result of the combination of fragments (macroradicals), which is characteristic of reactions of the polycondensation type. This effect is manifested even more explicitly in three-dimensional polymerisation of any type. The polymerisation results in the appearance of branched macromolecules carrying both active centres and 'suspended' functional groups; the reaction between them leads to the combination of macromolecules. Thus, in this case too the formation of macromolecules from fragments makes a significant contribution to the overall polymerisation process.

However, as a result of the effect of substitution in polycondensation, a considerable proportion of the monomer molecules may begin to fail to react with one another, adding instead to the polymer chains. For example, this may be the result of the process occurring in accordance with Scheme (26) if $k_2 \gg k_1, k_3$.

The principal disadvantage of the kinetic approach is the impossibility of calculating with its aid the structural characteristics of a network polymer (the gel fraction). The structure of the gel may be inferred to some extent from data obtained by analysing the sol fraction with the aid of the kinetic method^{3,62} but these conclusions are extremely indirect.

The full scale structural characteristics of the polymer, without limitations associated with the cyclisation reaction, can be found by the computer modelling of the formation reactions of polymers (see, for example, Refs 63–66). A satisfactory agreement between the data obtained by kinetic calculations and the results of modelling is then often attained.⁶⁷ However, in the present review we shall not be concerned with this approach, which is fairly specific as regards method and object of study.

III. Statistical methods

The structural characteristics of the polymer in any state can be established by statistical methods. A simple approach, based on the application of statistical calculations, was first proposed by Flory.¹¹ Combinatorial computational methods for the determination of the MMD function in the case of *f*-functional polycondensation were already used in classical studies.^{11,68} Later, in the 1960s–1970s, a formalised and therefore simpler and elegant method, based on the theory of branching processes (see the detailed survey in the monograph of Irzhak *et al.*³), was proposed for such calculations. Attempts were made to use this method in order to solve virtually any polycondensation problem, including

represent the bonds and atoms (units) joined by these bonds. The complete set of concentrations of all the blocks G characterises unambiguously the composition and structure of the system. In this sense, the concentration $y(G)$ is analogous to the MMD function of the polymer.

Speaking of ‘bonds’, we have in mind those bonds which are formed as a result of the reaction considered. Consequently the concept of bond blocks is closely related to the chemistry of the process. Each bond is characterised by groups (units) which are joined by this bond: the bond $a-a$ joins the units A , the bond $a-b$ joins the units A and B , *etc.* In other words, the designations of different units have only the significance of a feature (characteristic) of the bonds.

We shall elucidate the significance of the concept of bond blocks in relation to a linear copolymer. As can be seen from Table 3, the chain may contain a large number of blocks (this number is naturally even greater in a set of chains) and larger blocks (for example, $a-a-b-b$) include smaller blocks ($a-a$, $a-b$, $b-b$, $a-a-b$, $a-b-b$). The complete set of blocks (Table 3 presents blocks containing not more than three bonds) characterises unambiguously the structure of the chain.

Table 3. The structure of the copolymer chain $a-b-b-a-a-a-b-a-a-b$ expressed with the aid of the bond block concept.

Bond block	Number of bonds in block	Number of blocks in chain
$a-a$	1	3
$a-b$	1	4
$b-b$	1	1
$a-a-a$	2	1
$a-a-b$ ($b-a-a$)	2	4
$a-b-a$	2	1
$a-b-b$ ($b-b-a$)	2	2
$a-a-a-b$ ($b-a-a-a$)	3	2
$a-b-b-a$	3	1
$a-a-b-b$ ($b-b-a-a$)	3	1

In a linear homopolymer, the bond blocks differ only in length, *i.e.* in the number of bonds constituting the block. Therefore the relation between the bond block concentrations (y_i) and the chain concentrations (x_i) assumes an extremely simple form:

$$y_n = \sum_{i=n}^{\infty} (i-n)x_i. \quad (41)$$

The multiplier $(i-n)$ is equal to the number of ways in which a block comprising n bonds can be accommodated in a chain containing i units. The quantity y_0 represents the overall concentration of monomer units in the system (they include both the units in the polymer and the free monomers, *i.e.* y_0 is a constant quantity), y_1 is the overall concentration of bonds, and y_1/y_0 is the degree of conversion.

The converse relation, which follows from Eqn (41), is also valid:

$$x_i = y_{i-1} - 2y_i + y_{i+1}. \quad (42)$$

The significance of Eqn (42) is most closely related to the very concept of bond blocks. Indeed, as can be seen from Table 3, large blocks include smaller blocks. Consequently the subtraction of the concentrations y_{i-1} from the concentrations y_i yields the concentration of the terminal block of the same dimension (i) and the same operation with the concentrations of terminal blocks makes it possible to find the corresponding concentration of chains by Eqn (42).

Condition (42) may be extended to chains (macromolecules) and blocks of any configuration.

Suppose that we have a bond block of size i (i is the total number of bonds) connected to the overall polymer system *via* n

terminal blocks (bonds). The concentration of blocks of the same configuration but with one ‘broken’ bond of type k (z_i^k) can be expressed as follows:

$$z_i^k = y_i - y_{i+1}^k = y_i(1 - y_1^k), \quad (43)$$

where y_{i+1}^k is the concentration of the block the size of which has been increased by one type k bond compared with the block of size i and y_1^k is the concentration of unit blocks of type k . The product corresponds to symbolic multiplication, *i.e.* the summation of indices (block sizes), just as in the usual multiplication the power exponents are added together.

Similarly for the concentration of blocks having the same configuration but with two ‘broken’ bonds, of types k and m , we obtain

$$z_i^{k,m} = z_i^k(1 - y_1^m) = y_i(1 - y_1^k)(1 - y_1^m). \quad (44)$$

Since the chain (macromolecule) containing $i+1$ units corresponds to a block with the same configuration and size i in which all n terminal bonds are ‘broken’, the overall expression assumes the form

$$x_{i+1} = y_i \prod_{j=1}^{il} (1 - y_1^j). \quad (45)$$

This postulate is illustrated below in relation to copolymer systems.

Thus there is an unambiguous reciprocal correspondence between the concentrations of bond blocks and the MMD of the chains.

It has been shown^{69,71,76,77} that kinetic equations can be formulated for bond blocks and the system of equations is complete in all cases: the concentration of a block of any length and complexity depends on the presence of only those blocks which do not surpass the block under consideration as regards length and complexity. This makes it possible to find by a numerical method the exact concentration of a block of any length and hence the exact concentration of the chains.

As an illustration, we shall quote data taken from Refs 76 and 77 (Table 4), where a direct calculation for the kinetic scheme (26) was carried out.

Table 4. Dependence of the relative error (δ_i) in the calculation of the concentration of chains x_i on the numerical values of the kinetic constants of Scheme (26) and on the number of equations (n) taken into account in the calculation ($k_1 = 1$).

i	k_2	k_3	δ_i			
			$n = 9$	$n = 19$	$n = 29$	$n = 49$
1	1	1	0.191	0.047	0.014	0.001
1	1	9	0.060	0.031	0.019	0.020
1	3	9	0.192	0.078	0.041	0.013
1	9	9	0.521	0.123	0.044	0.007
3	1	1	0.225	0.052	0.015	0.001
3	1	9	0.680	0.321	0.195	0.105
3	3	9	0.770	0.284	0.138	0.042
3	9	9	0.534	0.123	0.042	0.007
5	1	1	0.260	0.055	0.015	0.002
5	1	9	1.333	0.524	0.298	0.117
5	3	9	1.110	0.349	0.161	0.048
5	9	9	0.578	0.129	0.045	0.006
7	1	1	0.294	0.059	0.016	0.002
7	1	9	1.896	0.652	0.344	0.132
7	3	9	1.350	0.378	0.176	0.050
7	9	9	0.671	0.140	0.048	0.009
9	1	1	—	0.063	0.016	0.000
9	1	9	—	0.731	0.361	0.139
9	3	9	—	0.414	0.180	0.048
9	9	9	—	0.151	0.051	0.007

Table 4 presents the maximum relative errors δ_i in the calculation of x_i as a function of the number of equations taken into account in the numerical solution of the equations:

$$\delta_i = \frac{x_i - x_{ib}}{x_{ib}}, \quad (46)$$

where x_i is the concentration of the chains calculated on the basis of Scheme (26) and x_{ib} is the concentration of chains calculated by Eqn (42) using the concept of bond blocks and therefore independent of the number of equations considered.

The table shows that the deviations from the exact value may be considerable. At the same time, the employment of the concept of bond blocks makes it possible to find exact concentrations for any number of equations.

The possibility of the exact calculation of the bond block concentrations plays a most important role in the determination of the structures of copolymers. Indeed, the modern experimental methods make it possible to characterise the structure of a copolymer solely in terms of the number (concentrations) of blocks of not too great a size — diad, triad, tetrad.^{12, 72} On the other hand, the kinetic calculation of the structure in the usual version requires the consideration of copolymer chains of all possible configurations. This creates unsurmountable computational difficulties. Furthermore, for a sufficient length and a considerable number of components, the set of possible chain types becomes very large, comparable to the Avogadro number. This means that the number of molecules of each type is insufficient to ensure the operation of the statistical Law of Mass Action. I. M. Lifshits drew attention to this factor for the first time at one of the seminars on polymer physics at Moscow State University. This difficulty disappears when the concept of bond blocks is used in the calculations.

In the formulation of kinetic equations for the calculation of the concentrations of bond blocks, an extremely simple rule is employed: all possible ways in which the given structure can be formed are added together. The concept of the terminal block, which is an extension of the concept of a functional group, therefore assumes key importance in the consideration of kinetic problems in the language of bond blocks. Indeed, as a result of the reaction between functional groups, one bond or, in other words, a bond block of unit length is formed. If a functional group with units attached to it (one, two, and more) is considered, then one may be dealing with the formation of a larger structure, *i.e.* a larger bond block. For example, the reaction between the functional groups $\sim a + \sim b$ leads to the appearance of the bond $\sim a-b\sim$. The following reactions participate in the formation of the block $\sim aabba\sim$:



The formation of terminal blocks with a complex structure, for example $\sim aabb$, is also associated with the occurrence of a series of reactions:



etc. However, as can be seen, all the reactions proceed with participation of reactants the structure of which is not more complex than that of the bond block being sought. Thus the system of equations is closed and the experimental requirements determine in relation to which blocks the kinetic problem is to be

solved. This in fact constitutes the advantage of the approach based on the concept of bond blocks.

Analysis of the structure of the system of kinetic equations describing the bond block accumulation processes^{71, 77} showed that it may be subdivided into groups of equations in such a way that the concentrations of the structures described by these equations are susceptible to direct calculation. The concentrations of larger structures are found by probability computational methods. If the minimum size of a block corresponds to one bond, we arrive at the case of the absolute application of statistical methods. It is almost always possible to identify such structures of minimum size from which any structural formations, however large and complex, are made up. The use of the concept of bond blocks makes it possible to simplify still further the solution of kinetic problems, since it becomes unnecessary to formulate differential equations for blocks of all sizes: it is sufficient to solve these problems for elementary blocks, using statistical calculations for larger formations. In other words, this method combines the advantages of both the kinetic and the statistical approaches.

It was found that the criterion of 'being elementary'^{71, 77} is the absence of the influence of the effects of substitution on the reactivity of the functional groups on the other hand, within an 'elementary' block, these effects do occur. We shall elucidate this postulate by a simple example.

Suppose that a copolycondensation reaction takes place between units carrying functional groups of types A and B and there is a possibility of both A + A and A + B interactions, on the one hand, and B + B interactions, on the other, the effect of substitution in the first sphere being observed in groups A, while in groups B there is no such effect. The reaction results in the formation of blocks of different structure:



In order to calculate blocks of all these types, one has to begin with differential equations describing their formation. However, in more complex blocks, for example $\sim ba...abbba...ababbabb\sim$, it is possible to differentiate smaller blocks $\sim ba...b\sim$, $\sim b\sim$, $\sim bab\sim$, which are 'elementary', and from which the entire block is constructed in accordance with the laws of probability. If, as in the case of homopolycondensation in the presence of effects of substitution, it is not possible to differentiate such elementary blocks, the statistical approaches are found to be completely unsuitable.¹³

As an illustration, we shall calculate the MMD for the chains of a polymer formed as a result of the reaction between the monomers AA and BB, the substitution effect being observed in the former but not in the latter. This scheme corresponds, for example, to the reactions between phenylene diisocyanate (AA) and a diol (BB) and between an amine (AA) and a diepoxide (BB).

The formation reactions of the corresponding bond blocks can be represented in the form



Component a includes functional groups belonging to the initial monomer AA and $\sim a$ is a terminal block of the polymer chain. Since there is no substitution effect in group B, there is no need to differentiate groups B belonging to different molecules. For this reason, b includes any terminal blocks belonging both to the initial monomer BB and to polymer chains. In the general case, the kinetic constants are not equal to one another and

$$\frac{k_2}{k_1} = r \neq 1.$$

The solution of the system of equations describing scheme (49) leads to the following relations:

$$\begin{aligned}
\alpha_A &= 1 - \frac{e^{-r\tau} - (r-1)e^{-2\tau}}{2-r}, \\
\alpha_B &= Q\alpha_A, \\
p_{AB} &= 2 \frac{e^{-r\tau} - e^{-2\tau}}{2-r}, \\
p_{BA} &= 2\alpha_B(1-\alpha_B), \\
p_{BAB} &= \frac{2rQ}{2-r} \left(\frac{1-e^{-r\tau}}{r} - \frac{1-e^{-2\tau}}{2} \right).
\end{aligned} \quad (50)$$

Here α_A and α_B are the conversions of the corresponding groups, Q is the initial ratio of the functional groups A and B, p_{AB} , p_{BA} , and p_{BAB} are the probabilities (relative concentrations) of the terminal bond blocks $\sim ba\sim$ and $\sim ab\sim$ and of the block $\sim bab\sim$ (including both terminal and inner blocks) respectively, and τ is the fictitious time:

$$\tau = \int k_1 b dt. \quad (51)$$

The concentrations of the chains AA, BB, AB, ABA, and BAB are calculated on the basis of the kinetic scheme. The concentrations of larger chains are determined with the aid of relations, analogous to Eqn (42), namely

$$\begin{aligned}
x\{(BA)_i B\} &= y\{(BA)_i B\} - 2y\{A(BA)_i B\} + y\{A(BA)_i BA\}, \\
x\{A(BA)_i B\} &= y\{A(BA)_i B\} - y\{BA(BA)_i B\} - y\{A(BA)_i BA\} + \\
&\quad + y\{BA(BA)_i BA\}, \\
x\{A(BA)_i BA\} &= y\{A(BA)_i BA\} - 2y\{BA(BA)_i BA\} + \\
&\quad + y\{BA(BA)_i BAB\}.
\end{aligned} \quad (52)$$

The concentrations of the blocks $y\{\dots\}$ are determined in accordance with the probability relations:

$$\begin{aligned}
y\{(BA)_i B\} &= (y\{BAB\})^i = (p_{BAB})^i, \\
y\{A(BA)_i B\} &= (y\{BAB\})^i y\{BA\} = (p_{BAB})^i \alpha_B, \\
y\{A(BA)_i BA\} &= (y\{BAB\})^i (y\{BA\})^2 = (p_{BAB})^i (\alpha_B)^2.
\end{aligned} \quad (53)$$

Thus

$$\begin{aligned}
x\{(BA)_i B\} &= B_0 (1-\alpha_B)^2 (p_{BAB})^i, \\
x\{A(BA)_i B\} &= 2B_0 \alpha_B \left(1 - \frac{p_{BAB}}{\alpha_B}\right) (1-\alpha_B) (p_{BAB})^i, \\
x\{A(BA)_i BA\} &= B_0 (\alpha_B)^2 \left(1 - \frac{p_{BAB}}{\alpha_B}\right)^2 (p_{BAB})^i.
\end{aligned} \quad (54)$$

When the equality of the kinetic constants ($r = 1$) holds then $p_{BAB}/\alpha_B = \alpha_A$ and Eqns (54) lead to simple probability formulae.

The indices [subscripts] correspond to the type of end groups in the chain the length of which i is equal to the number of BA bonds contained in it.

Figure 5 presents the concentrations of the BAB molecules found in three ways: by the direct kinetic calculation, by the probability calculation employing kinetic data on the conversion of groups A and B (α_A and α_B respectively), and by the calculation employing bond blocks (the $\{BAB\}$ block). Evidently, in the absence of the substitution effect (when the constants are equal), all three methods yield concordant results. If the rate constants for the first and second additions are different, only the results of the direct kinetic calculation and the calculation based on the concept of bond blocks agree. The statistical calculation leads to an incorrect result.

The concentration of small molecules can be readily calculated. Problems arise with larger structures.

The algorithm of the procedure for the description of the structure of a network polymer, formed, for example, in the

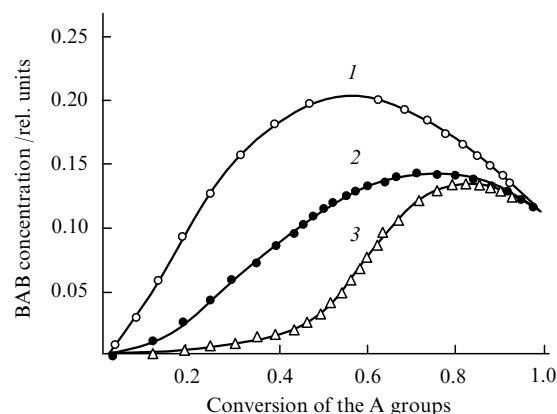
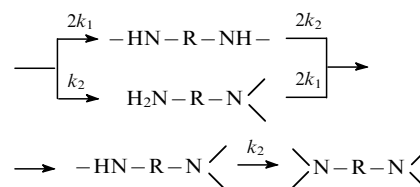


Figure 5. Variation of the concentration of the molecules BAB during the AA + BB copolycondensation process occurring in accordance with Scheme (49): (1) direct kinetic calculation (curve) and calculation based on bond blocks (symbols) with $r = 10$; (2) kinetic calculation with $r = 1.0$ and statistical calculation with $r = 10.0, 1.0$, and 0.1 (curve) as well as calculation based on bond blocks with $r = 1.0$ (symbols); (3) direct kinetic calculation (curve) and calculation based on bond blocks (symbols).

interaction of a diepoxide with a diamine [Eqn (40)], reduces in the general case to the following.

1. The bond block concentrations are calculated kinetically in conformity with Scheme (55) (on the assumption that the substitution effect occurs only for the amine but not for the epoxide oligomer).



2. The statistical calculation is performed for any structural fragments bearing in mind that the $H_2N-R-NH_2$ molecule enters exclusively into the sol fraction of the polymer system, $H_2N-R-NH-$ is the end group of the chains, and $-HN-R-N \begin{array}{c} \diagup \\ \diagdown \end{array}$ and $\begin{array}{c} \diagup \\ \diagdown \end{array} N-R-N \begin{array}{c} \diagup \\ \diagdown \end{array}$ are network nodes.

Thus the use of bond block data in the calculation makes it possible to solve structural problems effectively.

V. Conclusion

We have endeavoured to show that modern methods for the solution of Eqn (1) make it possible to answer all or the majority of formal kinetic questions. Naturally, the most important predictive problems, namely how and under what conditions the process should be carried out in order to obtain a polymer with a specified structure, remained outside the scope of our review. Its subject was only the establishment of a direct relation between the structure of the polymer and the kinetic parameters of the polycondensation process. Evidently, the problems of reactivity should be considered from completely different standpoints. This constitutes another field of science. If, as stated above, real processes are complicated by a possible change in the physical state of the system in the course of the reaction, which alters not merely the numerical values of the kinetic constants but the very process mechanism, then evidently the attempts at prediction become extremely problematical. Certain approaches to the solution of this problem have already been developed to some

extent (for example, attempts to take into account the vitrification of the system are known), but they are either too formal and require physical justification or are speculative and require a broad experimental test.

Reactions between rigid-chain macromolecules,^{80,81} particularly in liquid crystal polymer systems,^{82,83} carried out in order to obtain network polymers from them are nowadays of special interest. In this case the low flexibility of the chains — the carriers of functional groups — necessitates the formulation of more general questions: about the nature of the collisions of the reaction centres, about the influence of chain length on the reactivity, about the influence of the organisation of the medium on the kinetic parameters of the processes, etc. These problems still await their investigators.

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Polytype formation in nonmetallic substances

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Abstract. A systematic account is given of the known data on polytypism in nonmetallic substances with various structures. The existing hypotheses concerning the nature of polytypism are discussed. It is shown that polytype formation in nonmetallic crystals is a solid-state relaxation rearrangement accompanied by the formation of planar defects of various types, inducing the breakdown in the periodicity of the packing of atomic layers. Such defects and hence structural elements of polytypes may be structural (growths, deformation) and chemical packing defects, microtwins, antiphase boundaries, layers of vacancies, as well as layers of other phases coupled coherently with the basic structure. For diamond-like phases (SiC, AlN, BN), intragranular polytype transformations, induced by the migration of boundaries, occur together with intragranular polytype transformations. The bibliography includes 294 references.

I. Introduction

As a property of crystalline solids, polytypism is determined by the possibility that a given substance may exist as a multiplicity of structural forms differing in the packing of identical layers, which are structural elements of the basic lattice. Whereas the characteristic of the latter is the interlayer distance (c_0), the characteristic of the polytype lattice is the distance between blocks (C), which consist, of several layers (n) of the basic lattice:

$$C = nc_0.$$

When n is an integer, one is dealing with commensurate polytypes, while in the case of fractional n the polytypes are noncommensurate.

In terms of the type of ordering, polytypes can be divided into two kinds: ordered polytypes with a distinct repeatability of the blocks and non ordered polytypes [one-dimensionally disordered state (ODS)] distinguished by the fact that the blocks with different C are arranged in a random fashion, *i.e.* without periodicity.

A multiplicity of ways of designating polytypes, reflecting their structure, are known.^{1–3} The Ramsdell designations are

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most often employed as the simplest and clearest. The designation includes the number of layers in the unit cell and a letter indicating the type of symmetry of the cell: H — hexagonal, R — rhombohedral, T — trigonal. For example, 6H is a polytype with a six-layer repeat period along the c axis and a primitive hexagonal cell. For rhombohedral polytypes, the number of layers is a multiple of three.

A new method of describing polytypes as structures with different numbers and types of regular systems of points has been proposed recently.⁴ Bokii and Laptev^{4,5} examined in detail the approach to this kind of description in relation to ZnS, CdI₂, TiO₂, and certain silicates. However, this method of describing polytypes has not as yet found extensive application.

For the majority of polytypes, the repeat period of the layers varies in one direction. For this reason, polytypism is frequently referred to as one-dimensional polymorphism.

Verma and Krishna² defined polytypism as the ability of a substance to crystallise in several different modifications and in all these modifications two unit cell parameters are identical, whilst the third is a variable integral multiple of the same quantity. The structural state of polytypes should also correspond to three essential conditions: firstly, polytypic forms must consist of identical structural units and differ only in the packing of the layers; secondly, each layer should have one chemical composition corresponding to the stoichiometric composition of the crystal; thirdly, each pair of neighbouring layers is equivalent. The foregoing refers to the classical definition based on the study of polytypism in ten single-crystal substances. The compounds examined include SiC, ZnS, CdI₂, PbI₂, CdBr₂, AgI, *etc.*, which had been regarded previously as strictly stoichiometric. The above definition of polytypism was formulated when noncommensurate polytypes had not yet been observed.

Extensive experimental data confirming the tendency towards polytype formation in crystalline solids differing in the types of chemical bonding, crystal lattice, the number of different atoms (substances ranging from monatomic, for example diamond and carbon, to pentaatomic and hexaatomic in minerals) have now accumulated. Accordingly, it has been established that polytypism is characteristic of various classes of substances: metals, ceramics, minerals, intermetallic compounds, and organic substances. It has been observed in the study of not only single crystals but also films, powder particles, and polycrystalline compact materials. Polytype formation is very often associated with the nonstoichiometry of substances. Nonstoichiometry in substances such as SiC,⁶ ZnS,⁷ CdS,⁸ *etc.* has also been discovered.

Thompson⁹ defined polytypism as a special kind of polymorphism in which new modifications arise as a result of different types of packing of structurally compatible units. In other words,

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polytypes are variants of the packing of simple elements characteristic of the basic structure. In contrast to the definition of polytypism given by Verma and Krishna,² in this definition the condition of the structural and chemical identity of the structural elements in the polytype is not obligatory.

In 1984, the Commission of the International Union of Crystallographers proposed a new definition: polytypism is 'the phenomenon of the existence of elements or compounds in the form of two or more multilayer crystalline structures differing in the sequence in which the layers are packed. The layers need not necessarily be crystallographically identical but they should be similar. Polytypism differs from polymorphism by allowing small differences between the chemical compositions of structures not exceeding 0.25 atom per formula unit of any constituent element. Layered structures which differ from one another to an extent greater than this are referred to as polytypoids rather than polytypes'.¹⁰ However, this terminology has not, found extensive application nowadays. As a typical example, one may quote aluminium nitride, for which a relation between composition and multilayer structures has been established. On the other hand, the latter are referred to as polytypes and rarely as polytypoids or pseudopolytypes.

Polytypism was first observed in 1912 by Baumhauer¹¹ in SiC single crystals. However, the study of this phenomenon did not begin until 1940. At the beginning of the 1950s, the first theory of polytypism appeared (Frank's theory). It referred to the formation of polytypes in the growth of crystals and was therefore called the growth theory. It was based on the hypothesis of the decisive role of screw dislocations in the formation of polytypes with different numbers of layers, in particular the hypothesis that the period of the polytype is determined by the height of the growth step. This theory described satisfactorily the appearance of short-period polytypes in the growth of crystals but could not account for the appearance of long-period structures. The first review of polytype formation in crystals, in which the above theory was also considered, was written by Verma and Krishna.²

Extensive data have now accumulated on the phenomenon of polytypism in crystalline solids of different classes and on the possible mechanisms of its occurrence. The physical and chemical nature of this phenomenon has aroused much interest as a fundamental property of crystalline solids. The practical aspect of this phenomenon is also important. The theoretical and experimental data available at present on polytypism indicate that this phenomenon may be determined by a multiplicity of factors. It is also evident that there cannot be a single mechanism of polytype formation. This is indicated also by the fact that the change in the lattice periodicity in crystals may be induced (as will be shown below) by the formation of planar defects of different nature — structural and chemical packing defects, growth and deformation microtwins, antiphase boundaries, layers of outcrops of other phases, layer-by-layer changes in the coordination numbers and packing motifs of the constituent atoms, *etc.*

The majority of data on polytypism in metallic materials, including pure metals (only the lanthanides), alloys, intermetallic compounds, including Laves phases (compounds of the type AB₂), and ordered alloys, have been surveyed in monographs^{3,12}. In these communications, Nikolin³ identified two kinds of polytypes: stable, formed on crystallisation or annealing at a high temperature, and unstable formed as a result of martensite transformations. For certain Laves phases and ordered alloys (for example in the Cu–Au, Ag–Mn, and Pd–Mn systems), a relation was discovered between the modulation period of long-period structures and the average number of valence electrons per atom, the so called electron concentration e/a (e is the total number of valence electrons and a the number of atoms in the unit cell). On the basis of these data, it was concluded³ that polytype formation in metallic crystals is determined by the band factor, *i.e.* by their band structure.

In recent years, the diversity of polytypic structures and their stability in crystalline solids have been considered on the basis of

the model description taking into account the competitive nature of the interaction between structural units (blocks or polyhedra), the different variants of the packing of which actually determine polytype formation, including two- and three-dimensional polytype formation. The Frenkel' – Kontorova and Ising (spin model) models are best known.^{13,14} The latter is based on the idea of the decisive role in polytype formation of the exchange interaction between the first and subsequent structural units as the basic elements of the crystal lattices of solids (the ANNNI model — Axial Next Nearest Neighbour Ising).

The principal postulates on which the model is based are as follows: polytypes are regarded as a series of different variants of the packing of structurally compatible modules (structural units); the structural units are formed on the basis of coordination polyhedra; the polytype formation and the stability of polytypes are a consequence of the change in the effective energy of the interaction between the structural units; the effective energy is a function of pressure, temperature, and chemical composition of the medium. The agreement, between the model considered and a real system has been demonstrated in relation to the polytypic structures of spinelloids. A satisfactory agreement is observed also for compounds such as SiC and ZnS.^{13–15} The possibility of applying this model to account, for the polytypism in solid solutions of metals with a hexagonal close-packed lattice has been demonstrated.^{16,17}

II. Polytypism in nonmetallic crystals

The available information about the polytypism in nonmetallic crystals having the compositions MX and MX₂ (SiC, ZnS, CdI₂, *etc.*), published up to 1966, has been surveyed.² Certain data on polytypes in minerals can be found in two communications.^{2,18} Extensive information about the polytypism in such materials has now accumulated.

Polytypism as a physical phenomenon in nonmetallic substances may be classified in terms of various features: the thermodynamic conditions under which it occurs, the type of planar defects inducing an ordered alternation of blocks of layers, the classes of substances with an identical type of chemical bonding or crystal lattice, and also the properties and applications of the substances. The classification taking into account the features specified constitutes an independent task. Bearing in mind the discovery of polytypism as a growth phenomenon and its subsequent observation in crystals obtained under various conditions, one may identify four groups of polytypism: growth, thermal, deformation, and concentration. The above terminology reflects the nature of the principal factor governing polytype formation, although in the majority of cases its development is determined by a combination of many factors. Furthermore, such subdivision is suitable only for the group of substances with diamond and diamond-like phase (wurtzite and sphalerite) lattices. The above kinds of polytypism occur in precisely these substances. For example, growth polytypism is characteristic of SiC, ZnS, C (graphite), C (lonsdaleite), Si, and CdS; thermal polytypism is characteristic of SiC, ZnS, and 2H BN, concentration polytypism is characteristic of SiC, ZnS, AlN, ZnO, BeO, and BeSiN₂, and deformation polytypism is characteristic of SiC, ZnS, CdS, C (diamond), 2H BN, 3C BN, and Si (the polytypes are formed on the basis of 3C and 2H phases for SiC, ZnS, and CdS, the 3C phase for Si, and the 2H phase for AlN, BeO, ZnO, and BeSiN₂). For other substances, the combination of such varieties of polytypism is not observed.

Since we shall subsequently discuss briefly also the practical aspect of polytypism in non metallic materials, it is useful to analyse the problem of polytypism as a whole for different groups of materials differentiated in inorganic chemistry as carbides, nitrides, oxides, *etc.* Henceforth we shall consider polytypism in individual groups of substances, but we shall note beforehand certain data on polytypism in organic substances and shall also describe the available information about this phenomenon in

monatomic substances; the polytypism in transition metal carbides and nitrides of the type of interstitial phases¹⁹ will be considered jointly.

The possibility of the formation of polytypes in organic substances was first pointed out by Verma and Krishna.² The direct observation of polytypes by high resolution microscopy in crystalline organic substances (in relation to phthalocyanine) has been reported by Howitt.²⁰ The formation of phthalocyanine polytypes was accompanied by the $\beta \rightarrow \alpha$ shear transformation. Zorkii and Nesterova²¹ observed intralayer polytypism in the selenium-containing organic substances $C_{16}H_{16}O_4Se$ and $C_{13}H_{10}N_4Se$. Its characteristic feature is that blocks having identical outer layers and differing in the structure of the 'core' arise in the structure of the initial substance. As a result, there is a possibility of the formation of homolayer (made up of identical layers) and heterolayer (made up of different layers) structural fragments.

1. Monatomic substances

Silicon and carbon belong to the class of monatomic substances tending to exhibit polytypism. Polytype formation in germanium has been mentioned²² but we are not aware of any concrete information.

a. Silicon

Silicon polytypes have been observed in an electron microscope study of its formations in the form of whiskers and fibres obtained by the decomposition of SiH_4 at 500–520 °C on gold-covered silicon supports.²³ The experimental and calculated unit cell parameters are virtually the same for the identified polytypes.

Polytype	6H	27R	51R	141R
$c(\text{calculation})/\text{\AA}$	18.84	84.65	159.89	442.05
$c(\text{experiment})/\text{\AA}$	18.59	84.61	160.07	442.29

The formation of polytypes on deformation of silicon is apparently also possible. This is indicated by data on the intense disordering of the Si structure with the diamond lattice on impact application of a load and the formation on subsequent annealing of the 2H modification from this structural state.²⁴ Data on the 3C $\rightarrow$ 2H transition in silicon at a high pressure²⁵ and following the application of a concentrated load, *i.e.* under the indenter,²⁶ are available. The above transition occurs also when a large number of arsenic ions are implanted in a silicon support.²⁷

b. Carbon

Three polymorphic modifications — graphite, lonsdaleite (hexagonal diamond), and diamond — are characteristic of crystalline carbon. They all tend to form polytypes.

The commonest polytype for graphite is 3R; the formation of polytypes 6R, 10H, and 12H is also possible.^{28,29}

The formation of a mixture of multilayer polytypes (MP) in lonsdaleite deformed at high pressures and temperatures ($T = 1800$ °C, $P = 7.7$ GPa) under conditions involving the formation of a polycrystalline diamond material has been observed in microdiffraction studies.³⁰ The presence of MP was indicated by a system of point reflections on continuous $h0l$ rows on the electron microdiffraction pattern of sections of the type (1120) through lonsdaleite particles. Subsequently the 6H polytype of lonsdaleite, formed on deposition of carbon films from the gas phase, was identified by electron microscopy.³¹ Calculated X-ray diffraction data for a series of lonsdaleite polytypes (3C, 2H, 6H, 4H, 8H, 10H, 15R, and 21R) have been published.³²

The possibility of the formation of MP from cubic diamond is indicated by the studies of Britun *et al.*³³ The presence of a set of nonsystematic point reflections (in rows parallel to 111) on the electron diffraction pattern of the {110} sections of diamond grains deformed at $T > 2200$ °C and $P = 8$ –10 GPa has been established. The density of the disperse twins on one plane of the

type {111} on the diffraction pattern, extending from boundary to boundary, is usually high in grains of this kind. These twins are formed as a rule only on deformation.

In the crystallisation of carbon from the gas phase, the regraphitisation of diamond, and laser irradiation of graphite, a variety of the carbon phase is formed — carbynes. Carbynes are regarded as linear carbon polytypes.³⁴ Such structures have been classified on the basis of various parameters: the linear relation between the number of atoms in the chain and the length of the c axis, the unit cell volume, and the ratio a/c .

2. Silicon carbide

It was noted above that SiC was the first substance in the study of which polytypism was observed as a physical phenomenon.¹¹ So far more than 150 polytypes with hexagonal, rhombohedral, and tetragonal symmetries have been identified in SiC. The parameter c in these polytypes varies from 0.5 nm for 2H to 1200 nm for 4680R. The polytypes observed up to 1966 have been described by Verma and Krishna² and data on polytypes found later are contained in papers published in periodicals.

The SiC polytypes are distinguished by the ratio of the carbon and silicon concentrations and hence by the X-ray density and the concentration of vacancies (Table 1). The silicon concentration should be 70.05 mass% for stoichiometric SiC, while for 3C SiC it is 71.04 mass% and for 6H SiC it amounts to 70.7 mass%. The data obtained in studies of the nonstoichiometry in SiC have been surveyed.³⁵

The polytypic transformations in SiC may occur under different thermodynamic conditions: only on heating (both in an inert medium and in the presence of impurities dissolving in the lattice), on application of different types of load (rubbing at room temper-

Table 1. Characteristics of certain silicon carbide polytypes.

Polytype	D	q	[Si]/[C]	$10^{-20}N/\text{cm}^{-3}$		h/eV
				N_{Si}	N_C	
3C	0	0.74	1.046	2.0	2.3	2.2
8H	0.25	0.96	1.029	3.3	1.7	2.56
21R	0.29	—	—	—	—	2.77
6H	0.33	1.22	1.022	4.3	1.5	2.86
33R	0.36	—	—	—	—	—
15R	0.40	1.19	1.012	5.7	1.1	2.9
10H	0.40	—	—	—	—	—
27R	0.44	1.30	1.008	6.2	1.0	—
4H	0.5	1.37	1.001	7.1	0.7	3.1

Note. The following designations have been adopted: D = degree of hexagonality, q = effective charge on the silicon atom, N = concentration of vacancies, h = width of the forbidden band. The forbidden band widths have been taken from Knippenberg³⁶ and the remaining parameters from Tsvetkov⁶.

ature, treatment by application of heat and pressure, bending, and a concentrated load under the indenter), and under the conditions of the implantation of impurities and subsequent annealing. Thus all known types of polytypism, occurring in the group of diamonds-like phases, are characteristic of SiC.

A multiplicity of publications have been devoted to the polytype formation in SiC during growth and also partly during post-heat treatment (see, for example, Refs 2 and 36–40). We shall deal briefly only with questions of the stability of the basic polytypes, including those arising on doping and deformation.

The two-layer (2H) wurtzite SiC phase is known, but its formation during growth and treatment is rarely observed. This form was first noted in the gas-phase deposition of SiC at 1400–1500 °C in hydrogen.⁴¹ Subsequently it was identified in combination with 3C SiC on nitrogenation of powdered silicon

pellets placed on a graphite support⁴² and also on decomposition of Si_3N_4 in nitrogen with an admixture of CO .⁴³ The stabilisation of the 2H SiC phase has been explained by the dissolution of oxygen.⁴⁴ Under the conditions of uniaxially oriented [slip along the (0001)⟨10 $\bar{1}$ 0⟩ system] application of a load to SiC crystals at 1600–1800 °C, transitions from the 6H and 3C phases to the 2H phase are possible.⁴⁵

The formation of the 2H phase is also observed in polycrystalline materials formed from SiC in the presence of oxygen and also aluminium or magnesium.^{46,47} This phase is extremely unstable. Its transition to the ODS or the two-phase (2H + 3C) state, characterised by a high concentration of packing defects (PD), occurs already at $T > 400$ °C.⁴⁸

The 3C SiC form is assumed to be stable at $T < 1400$ °C. At higher temperatures (both in the presence of impurities such as B and Al and without them), it is converted into the 6H polytype. The 6H polytype is the high-temperature ($T > 2000$ °C) stable form of SiC in an inert gaseous medium. This has been confirmed convincingly in a study³⁶ where it was established that the 6H polytype is formed in greatest amount in the synthesis of SiC from SiO_2 and C in the range 2000–3000 °C.

Numerous studies (see, for example, Refs 49–52) have shown that the aluminium and boron impurities (in the form of elemental phases or the compounds Al_2O_3 , B_4C , and BN) promote the $3\text{C} \rightarrow 6\text{H} \rightarrow 4\text{H}$ and $3\text{C} \rightarrow 4\text{H}$ transitions. The conversion into the 4H polytype occurs at $T > 1800$ °C; at $T > 2000$ °C, this polytype becomes dominant. It has been suggested that the aluminium and boron impurities stabilise the 4H polytype. The action of the above impurities is most effective in combination with added carbon. According to Tajima and Kingery,⁵³ aluminium and boron dissolve in the SiC lattice with formation of substitutional solid solutions and boron can substitute both silicon and carbon. The positive role of carbon in the polytypic transitions in SiC has been explained⁵⁴ by the operation of two factors: the removal of the oxygen film from the surface of the crystals and the increase in the concentration of vacancies.

The transitions between the 3C and 6H phases, occurring within crystallites under different conditions (only on heating, on heating accompanied by doping, and on deformation), occur in most cases *via* a series of heterophase ($3\text{C} + 6\text{H} + \text{MP}$) states differing in the number of phases. The individual phases and polytypes are represented by plates limited by close-packed (111) and (0001) planes, which determines the microdomain structure of the heterophase crystals (Fig. 1). Monopolytypic crystals can form only after prolonged annealing: for example, in the $3\text{C} \rightarrow 6\text{H}$ transition which is of the single crystal of the initial phase $\rightarrow$ single crystal of the final phase type.⁵⁵ A similar transition has been observed also in the transformation of 2H SiC in the form of whiskers into a lamellar single crystal of the 3C phase.³⁷

Numerous data indicate that nitrogen stabilises the 3C phase. This is manifested by the fact that, during the annealing of 3C SiC even at 2600 °C under nitrogen pressure ($66.5 \times 10^3 \text{ N m}^{-2}$), the

transformation to multilayer structures does not occur.⁵⁶ In the case of the initial 6H phase, the $6\text{H} \rightarrow 3\text{C}$ transformation takes place on annealing under nitrogen pressure [$(0.1 - 3) \times 10^6 \text{ N m}^{-2}$ (Jepps and Page)⁵⁷ and $4 \times 10^6 \text{ N m}^{-2}$ (Kieffer and Gugel)]⁵⁸ and also on hot pressing in the presence of added nitrides.⁵⁹ The formation of the 3C phase is then accompanied by the appearance of twins in the latter.

The $6\text{H} \rightarrow 3\text{C}$ transformation occurs also during annealing above 2000 °C in a silicon-containing medium⁵⁵ as well as on deformation. In the latter case, this is possible on rubbing at the normal temperature,⁶⁰ on uniaxial loading in the range 1800–2000 °C,⁴⁵ and at a high pressure (1–10 GPa) starting from a temperature of 400 °C.^{61–63} Britun *et al.*⁶⁴ established for the first time that this transformation is reversible at $P = 7.7$ GPa and $T > 2000$ °C. The direct $6\text{H} \rightarrow 3\text{C}$ and reverse $3\text{C} \rightarrow 6\text{H}$ transformations in the grains are crystallographically similar: the close-packed planes and directions in the initial final phases are parallel — (0001)∥(111); $[11\bar{2}0] \parallel [110]$.

The polytypic transitions in SiC take place also as a result of implantation. In most cases, marked disordering (the establishment of the ODS) or amorphisation take place after such a procedure. It is believed⁶⁵ that, on insertion of aluminium into epitaxial 6H SiC layers (at 1400 °C), the $6\text{H} \rightarrow 3\text{C}$ transformation occurs. It has been suggested that this is achieved *via* a disordered state. The formation of a twinned 3C phase has been observed after the post-annealing of the 4H + 6H crystals with implanted nitrogen.⁶⁶ It is believed that, on implantation of copper in the SiC ceramic, a polytypic transformation in the surface layers also takes place.⁶⁷ It has been established⁶⁸ that the implantation of boron and aluminium ions in the surface layers of 6H SiC crystals from the side of the (0001) plane leads to amorphisation. On subsequent annealing, a mixture of the 6H + 3C phases or only the 3C SiC phase is formed depending on the irradiation dose and temperature.

The study of polytypism began more than 50 years ago with the investigation of silicon carbide. However, hitherto the nature of the polytypism in SiC has not been established. There are numerous theories, hypotheses, and simply views on this question. We shall only indicate the principal ideas underlying the treatment of the polytypism in SiC.

The first (dislocation) theory of the polytypism in SiC (and of the phenomenon as a whole) has been proposed by Frank. It is based on the idea of the decisive role of screw dislocations in the formation of polytypes during the growth of crystals. Since this theory was first published jointly with Burton,⁶⁹ it is associated also with his name. The polymeric theory of Ramsdell and Kohn explains the appearance of polytypes by the growth of crystals on various atomic (polymer) groups. According to Jagodzinski's thermodynamic theory, the nature of polytypism is accounted for by the vibrational entropy effect. Schneer considered polytypic transformations as second-order transitions on the basis of the available data concerning the energy differences between polytypes. According to Peibst, polytype formation is associated with the thermal vibrations in the structure of the growing crystal. Knippenberg drew attention to the differences between the widths of the forbidden band in the SiC polytypes and therefore concluded that the electron energy plays a decisive role in polytype formation. The above theories have been examined in detail by Verma and Krishna.²

In the subsequent attempts to account for the polytypism in SiC, a decisive role was attributed to the structural packing defects generated in the transformations in the solid state during periodic slip or creep dislocations⁷⁰ and also those arising at the site of contact between the layers of polytypes growing at the boundary of the twinned crystals of the 3C phase.⁷¹ Direct confirmation of the decisive role of packing defects and twinned crystals of the 3C phase along the (111) plane in the $3\text{C} \rightarrow 6\text{H}$ transition in crystals has been obtained in an electron microscope study of thin foils.⁷²



Figure 1. The structure of the heterophase (6H + 3C + MP) SiC crystal.

Data on the energy of the packing defects (EPD) along the (0001) plane are available only for 6H SiC. They are extremely scattered: from 1.9 ± 0.25 ⁷³ to 13.00 ,⁷⁴ $45-65$,⁷⁵ and 72 ± 34 mJ m^{-2} at 20°C .⁷⁶ It has also been established⁷⁶ that the EPD of the 6H SiC phase increases with increase in temperature from 0.4 mJ m^{-2} at 1100°C to 0.45 ± 2 mJ m^{-2} at 2000°C . No information is available about the influence of impurities and deformations on the EPD. However, our studies indicate that the polytypic transformations on doping 6H SiC crystals with boron and aluminium and also on deformation by the application of a high pressure ($P = 4-10$ GPa at $1200-2000^\circ\text{C}$) are always preceded by the appearance of a high concentration of basic packing defects. The latter are a diagnostic sign of a decrease in the energy of the packing defects. The relation between the probability of the formation of the packing defects (α) and the EPD (γ) assumes the following form:⁷⁷

$$\alpha = \frac{Gb^2h\rho}{24\pi\gamma},$$

where G is the modulus of shear, b is the Burgers vector, h is the interplanar spacing, and ρ is the density of dislocations.

It has been suggested that the polytypes in SiC can be formed as a result of martensite transformations.⁶ However, experimental confirmation of the operation of this mechanism has not been obtained.

It has been suggested that the hexagonal SiC polytypes be regarded⁷⁸ as a twinned 3C phase with different concentrations of twinned crystals. Twinned crystal seams in such a phase consist of 2H SiC layers. On this basis, all polytypes (with the exception of 2H) may be regarded as phases differing in the amount of 3C SiC. The 3C SiC content in different polytypes varies from 50% to 75%; the greatest amount of 3C SiC (75%) is present in the 8H polytype. Similar ideas concerning the structure of polytypes with different numbers of layers had been put forward earlier by Ramsdell,⁷⁹ who suggested that multilayer polytypes are formed from basic 6H and 15R structures as a result of the breakdown of the packing periodicity in the latter. Data on the structures of long-period SiC polytypes, obtained in electron microscope studies of crystals by the direct lattice resolution method may serve as confirmation of these ideas. According to the results of Dubey and Singh,⁸⁰ the 126R polytype consists of blocks of rhombohedral polytypes with a smaller number of layers — 33R, 32R, and 48R, formed on the basis of the 6H, 15R, and 12R cells. It has been established⁸¹ that the 201R polytype is formed from the 6H, 15R, and 8H cells.

As already mentioned, the polytypism in SiC has been treated on the basis of the ANNNI model.¹⁵ Cheng *et al.*⁸² later developed a new approach in order to explain the appearance of SiC growth polytypes as equilibrium phases. It is based on the model of the long-range interaction between layers controlled by the background lattice energy. The principal factor is then the postulate that all polytypes may be formed as a result of different types of packing of diatomic SiC layers in the [111] direction of the 3C modification.

Analysis of data on the polytypic transformations in SiC crystals on heating and primarily under doping conditions demonstrates the important role of point defects. Indeed, in most cases (with the exception of heating in N_2) the $3\text{C} \rightarrow 6\text{H}$ transformation takes place. In the initial 3C structure there is an excess of silicon and hence of carbon vacancies (Table 1). Impurities which actively influence the polytypic transformations in SiC dissolve in the SiC lattice also with formation of vacancies. Evidently, on dissolution of B, Al, and N in SiC, heterovalent substitution occurs. The charge compensation in the lattice is then ensured by the formation of vacancies in one of the SiC sublattices⁸³ and the formation of complexes on the basis of the vacancies is inevitable.[†] If the vacancies as constituents of the SiC structure participate in polytype formation, the above process may be considered from the standpoint of nonstoichiometry *i.e.* as a transformation in a

AlN solid solution. An indirect, confirmation of this hypothesis exists. We have established that the $6\text{H} \rightarrow 4\text{H}$ (in the presence of boron or aluminium) and $2\text{H AlN} \rightarrow \text{MP}$ (*i.e.* a transformation in a AlN solid solution) transformations in polycrystalline materials are crystallographically and morphologically similar: the final polytypic structure is formed in a layer bounded by basal planes and enriched by the dissolved impurity (Fig. 2).

We may note the characteristic features of the $3\text{C} \rightarrow 6\text{H}$ and $3\text{C} \rightarrow 6\text{H} \rightarrow 4\text{H}$ transformations in polycrystalline SiC materials which we established. The transitions occur not only within but also between the grains in the stage involving the recrystallisation enlargement of the grains.

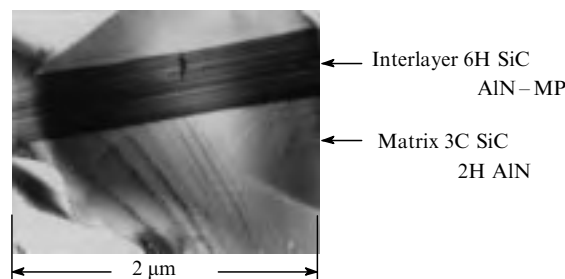


Figure 2. The substructure formed in the SiC and AlN crystals in polytypic transitions (in 6H SiC $\rightarrow$ 4H SiC under conditions involving doping with boron, in AlN in the course of the transition $2\text{H AlN} \rightarrow \text{MP}$).

In the first case, they are crystallographically oriented: under these conditions, the final polytype (it is usually formed in combination with MP in the initial stage of the transition) is segregated in the form of a single plate ($0.5-1$ μm thick) intersecting the grain from boundary to boundary (Fig. 2). The shape factor for such a plate (the ratio of the length l to the width d) can reach $10-20$. The plate is bounded by the basal planes and is coupled *via* these planes to the matrix (initial) phase. The formation of such structural states in the grains induces their anomalous growth and subsequently also the appearance of the grains of the final phase in the form of plates. In the course of the growth of the grains, polytypic transformations of the second type, characterised by the migration of the boundaries between grains made up of different polytypes, occur. Bearing in mind the nature of the mass transfer, determining the migration of the grains, one can postulate that such transformations take place *via* a diffusion mechanism. Fig. 3 presents schemes for the changes in the microstructure of the SiC materials obtained under the conditions of the polytypic transitions indicated. Evidently, depending on the structure of the growing grain, not only forward but also reverse ($6\text{H} \rightarrow 3\text{C}$ and $4\text{H} \rightarrow 6\text{H}$) transitions of the diffusion type may occur in the course of the collective recrystallisation. The evolution of the microstructural development of the SiC material in the case of such transitions is analogous to that observed in the AlN materials obtained in the $2\text{H AlN} \rightarrow \text{MP}$ transitions;⁸⁵ for SiC and AlN, these questions have been discussed in detail.⁸⁶ Such unusual shape formation in the subgrain structure and among the anisometric (lamellar) grains in SiC (as well as AlN), induced by polytypic transformations, promotes the formation of self-reinforced materials.⁸⁷

3. Aluminosilicon carbide

Two polytypes of aluminosilicon carbide, differing in the content of constituent atoms, are known: $8\text{H Al}_4\text{SiC}_4$ and $15\text{R Al}_2\text{Si}_2\text{C}_5$.

[†] The conclusion that such complexes are formed in SiC on dissolution of boron and aluminium has been reached⁸⁴ on the basis of data on the rate of diffusion of the above impurities in SiC.

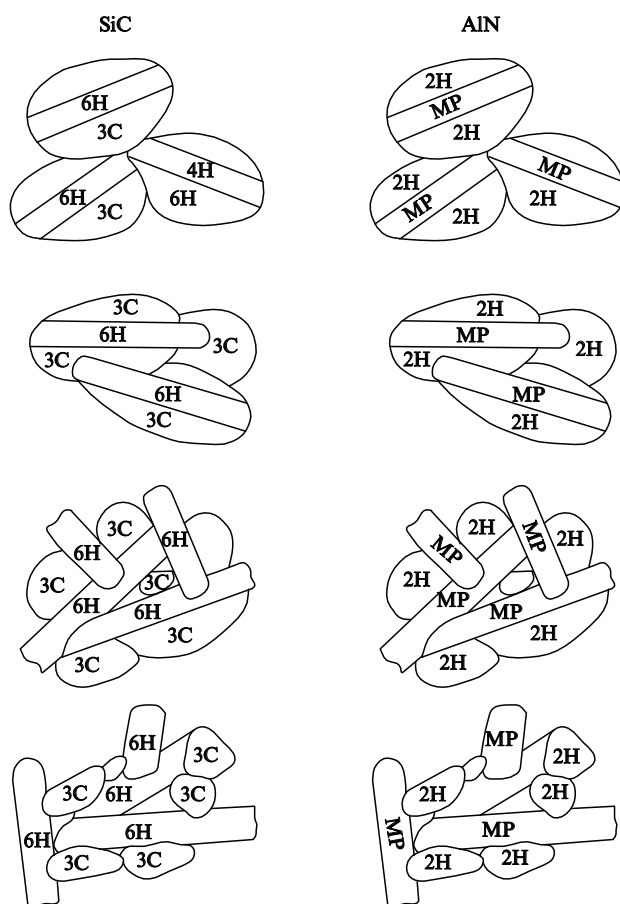


Figure 3. Variation of the granular structure during the development of intergranular polytypic transitions in SiC and AlN.

They have been detected in the products of the interaction of the AlC–SiC mixture⁸⁸ and the natural montmorillonite-polyacrylonite mixture.⁸⁹ The determinations of the cell size and of the interlayer distance led to the conclusion⁹⁰ that the structure of the aluminosilicon carbide may be produced by the substitution of AlN layers by SiC layers in carbonitrides of the type $\text{Al}_5\text{C}_3\text{N}$ and $\text{Al}_6\text{C}_3\text{N}_2$. The latter belong to the class of compounds with the general formula $(\text{AlN})_n\text{Al}_4\text{C}_3$ and are polytypic forms of aluminium nitride in the AlN–C system.⁹¹

The compounds $\text{Si}_3\text{Al}_5\text{N}_5\text{C}_3$ and $\text{Si}_3\text{Al}_4\text{N}_4\text{C}_3$ with the wurtzite lattice^{92,93} and $\text{Si}_3\text{Al}_5\text{N}_9$ ⁹⁴ are also known. However, despite the evident analogy with the structures in the Al–Si–C and Al–N–C systems, they are at present regarded as polytypes in the Si–Al–N–C system.

4. Boron carbide

Deformation polytypism is possible in boron carbide. This has been confirmed indirectly by data indicating the marked disordering in B_4C when the specimens are rubbed.⁹⁵ In the course of electron microscope studies of B_4C deformed at a high pressure and temperature ($P = 7.7$ GPa, $T = 1800$ °C) a similar disordering was also observed.⁹⁶ Furthermore, the formation of a mixture of MP was detected. It was established that the disordering is associated with the disperse twinning along one system of rhombohedral planes of the type $\{10\bar{1}1\}$.

5. Aluminium nitride

Among the nitrides, the most representative series of polytypes has been identified on the basis of aluminium nitride with the wurtzite structure (2H). AlN is represented by only this modification in the powders synthesised by various methods and in known

polycrystalline materials of all types. The AlN sphalerite phase has not been detected (in contrast to its crystallographic analogues — SiC, ZnS, BN, lonsdaleite, etc.). However, the formation of the AlN phase with a NaCl-type face-centred cubic lattice in microvolumes has been established. It is segregated (in the form of needles, plates with a rectangular cross-section) when nitrogenated iron silicide is annealed. Its unit cell parameter is in this case $a = 4.10$ Å. On heating above 600 °C, this phase is converted into the 2H form.⁹⁷ The face-centred cubic lattice of AlN may be formed from the 2H phase on application of high pressures in the course of static⁹⁸ and impact⁹⁹ compression. It has been noted¹⁰⁰ that the transition of AlN to the metallic state is possible at 90 GPa.

a. The Al–N–C system

The phenomenon of polytypism in aluminium nitride was first observed in the Al–N–C system in an X-ray study of single crystal specimens.¹⁰¹ The latter were obtained by recrystallising AlN via the gas phase at $T > 2000$ °C in a graphite crucible. The polytypes were identified in this case in the form of a series of carbonitride phases differing in their space groups (Table 2). These phases have been described⁹¹ as members of the $(\text{AlN})_n\text{Al}_4\text{C}_3$ AlC series ($n = 1–6$) — with the AlN and Al_4C_3 extreme members of the series. It was postulated that the structure of the carbonitrides can be represented as the combination of three types of blocks: $[\text{AlN}]_n$, $[\text{Al}_2\text{C}_2]_n$, and $[\text{Al}_2\text{C}]_n$. For example, the rhombohedral structure can be accordingly described by a set of blocks in the following sequence: $([\text{Al}_2\text{C}_2]_n[\text{AlN}]_n[\text{AlN}]_n[\text{Al}_2\text{C}]_n \cdot [\text{AlN}]_n[\text{AlN}]_n)_3$. This representation of the structure of the carbonitrides was later confirmed by the fact that the calculated (according to the model) and experimental unit cell parameters a and c agreed. The carbonitrides have also been described⁹¹ as multilayer structures in terms of Zhdanov's symbols (Table 2). The compositions Al_4C_3 and $\text{Al}_5\text{C}_3\text{N}$ correspond to the 9R⁸⁸ and 8H¹⁰² polytypes. The latter polytype is analogous to the 8H polytype in the Si–Al–O–N system.¹⁰² The analogy consists in the fact that the carbon atom substituting nitrogen in the case of the Al–N–C system in four nonmetallic layers has a coordination number of 6, whilst other nonmetallic atoms are located in distorted tetrahedra between octahedral layers.

Hitherto the communications of Jeffrey and Wu^{91,101} are the only ones in which the detection of multilayer structures in the AlN–C system has been reported.

b. The Al–N–O system

The polytype formation processes in AlN have been investigated in detail in a study of polycrystalline materials in the AlN– Al_2O_3 , AlN– SiO_2 , Si_3N_4 – Al_2O_3 –AlN, and Si_3N_4 – Al_2O_3 –AlN– SiO_2 systems. 2H AlN–O single crystals have been investigated only by

Table 2. Characteristics of the aluminium carbonitrides $(\text{AlN})_n\text{Al}_4\text{C}_3$ with $n = 0–6$ which are multilayer structures in the AlN–C system.^{91,101}

System	Space group	A	B	c/a	$l/\text{Å}$
Al_4C_3	$R\bar{3}m$	[13]	0012	7.474	2.074
$\text{Al}_5\text{C}_3\text{N}$	$P6mc$	[113]	0013	6.005	2.167
$\text{Al}_6\text{C}_3\text{N}_2$	$R\bar{3}m$	[1113]	0018	12.33	2.224
$\text{Al}_7\text{C}_3\text{N}_3$	$P6mc$	[11113]	0014	9.826	2.264
$\text{Al}_8\text{C}_3\text{N}_4$	$R\bar{3}m$	[111113]	0024	17.15	2.295
$\text{Al}_9\text{C}_3\text{N}_5^a$	$P6mc$	—	(0018)	(13.04)	(2.316)
$\text{Al}_{10}\text{C}_3\text{N}_6^a$	$R\bar{3}m$	—	(0030)	(21.97)	(2.333)

Note. The following designations have been adopted: A = packing sequence of the metal layers (Zhdanov's symbols are used); B = intence reflection in the 00 l row; l = interlayer distance. ^a Hypothetical phases.

Bartram and Slack.¹⁰³ It has been reliably established that the polytypes in such materials are formed on the basis of the AlN phase with the wurtzite structure and they are therefore referred to as the wurtzite polytypes. However, they are frequently referred to as sialone (in the Si–Al–O–N system) and oxynitride (in the Al–N–O system) polytypes. Evidently these names of the polytypes lack significance since sialones are solid solutions of aluminium and oxygen in the Si_3N_4 lattice of the phenakite type, while aluminium oxynitrides are compounds with a cubic spinel-type lattice.

Three kinds of sialones are known. The phases formed in the region located along the Si_3N_4 – $\text{AlN} \cdot \text{Al}_2\text{O}_3$ line (Fig. 4), for a fixed cation/anion ratio (M/X , where $M = \text{Al}$, Si and $X = \text{N}$, O) of $3/4$, are described by the general formula $\text{Si}_{6-x}\text{Al}_x\text{O}_x\text{N}_{8-x}$ (with $x \leq 4.2$) and are referred to as β' -sialones.¹⁰⁴ These phases have a β - Si_3N_4 lattice. For $x < 0.4$ and the ratio $M/X = 2/3$, phases with the orthorhombic lattice characteristic of Si_2ON_2 , are formed. They are described by the general formula $\text{Si}_{2-x}\text{Al}_x\text{O}_{2-x}\text{N}_{1+x}$ and are called O' -sialones.^{104, 105} Both kinds of sialones are formed on the basis of the β - Si_3N_4 lattice. α -Sialones are formed in the M – Si – Al – O – N ($M = \text{Li}$, Mg , Ca , Y , V , Nd , La) systems on the basis of the α - Si_3N_4 lattice. They are described by the general formula $\text{M}_x(\text{Si}, \text{Al})_{12}(\text{N}, \text{O})_{16}$ ($0 \leq x \leq 2$). The above metals M stabilise the Si_3N_4 α -phase.^{106, 107}

Aluminium oxynitrides with a spinel lattice are formed when the AlN content is in the range from ~ 45 mol.% to 25 mol.%.¹⁰⁸ Since the spinel has the formula AlON, it contains ~ 34.5 mol.% of AlN.¹⁰⁹ In the literature, the spinel is designated as AlON but it is also possible to encounter the term 'nitrogen-stabilised aluminium oxide'. The nonstoichiometric spinel $9\text{Al}_2\text{O}_3 \cdot \text{AlN}$, for

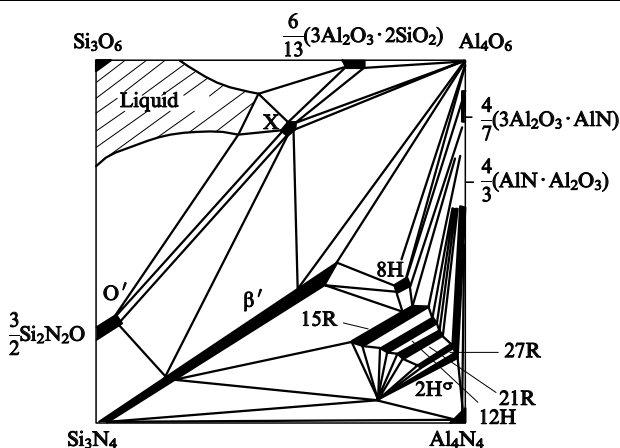
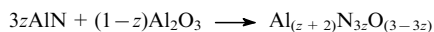


Figure 4. The isothermal section through the Si–Al–O–N diagram at 1750 °C.¹¹²

which there is a possibility of the formation of superstructures, is known.¹¹⁰ The spinel $\text{Al}_2\text{O}_3\text{N}$ is regarded as ideal. It may be obtained when the structural vacancies in Al_2O_3 are completely filled with nitrogen.¹⁰⁹ The phases in the AlN – Al_2O_3 system are formed by the reaction:¹⁰³



(this is pure AlN for $z = 1$ and pure Al_2O_3 for $z = 0$). A whole series of intermediate phases differing in the value of z have been noted. The range $0.889 > z > 0.25$ is characteristic of the oxynitride phases.

The communication of Lejus¹¹¹ about the formation of polytypes in the AlN – Al_2O_3 system must be regarded as the first in which a new phase was detected. Later this phase was identified¹¹² as the 21R AlN polytype. Japanese investigators detected the 2H AlN–O solid solution (the authors called it the 2H pseudopolytype) and the 27R, 16H, 21R, and 12H polytypes in a material based on AlN (the Al_2O_3 content, was up to 12.3%).¹¹³

Communications about the identification of the 20H and 27R polytypes⁹³ and the 12H, 27R, and 21R polytypes¹¹⁴ by X-ray diffraction appeared almost simultaneously. In the first case, they were detected in a study of the single crystals obtained in the course of the resublimation of AlN at $T \approx 2200$ °C in $\text{N}_2 + 5\%$ H_2 , whilst in the second they were detected in a study of a polycrystalline composition having the formula $5\text{AlN} \cdot 9\text{Al}_2\text{O}_3$. In the latter case, they were detected in the range of compositions where a liquid phase is formed in the Al–O–N system.

Kurdyumov *et al.*¹¹⁵ reported the formation of a 165R polytype on sintering a highly disperse AlN powder obtained by plasmachemical synthesis and containing ~ 2 mass% of oxygen. This polytype was detected in a 2H AlN grain in the form of a lamellar interlayer not containing other polytypes (Fig. 2).

In the course of an electron microscope study of a material having the composition AlN – Al_2O_3 , Krishnan *et al.*¹¹⁶ identified the 27R, 16H, and 32H polytypes; they observed the last polytype for the first time. In similar studies of a material obtained from AlN powder contaminated by oxygen as the accompanying impurity, the 33R and 20H polytypes were identified.¹¹⁷ According to the communication of Youngman and Harris,¹¹⁸ the 51R polytype, containing 6.6 at.% of oxygen, is formed in the AlN–O system. In the presence of MgO in this system, the formation of the 27R and 21R polytypes was discovered.¹¹⁹

Schuster¹²⁰ proposed a AlN – Al_2O_3 phase diagram based on the revised data of McCauley and Cowin¹¹⁴ in which the tentative regions corresponding to the formation of the 12H, 27R, and 21R polytypes were identified (Fig. 5).

c. The Si–Al–N–O system

The AlN polytypes were first observed as new phases in the Si_3N_4 – AlN – Al_2O_3 – SiO_2 system by Gauckler *et al.*¹⁰⁴ and Jack¹²¹ in the range of compositions with a high AlN content. These phases were represented¹⁰⁴ as Si–Al–O–N chemical compounds differing in the content of cations and anions. It was

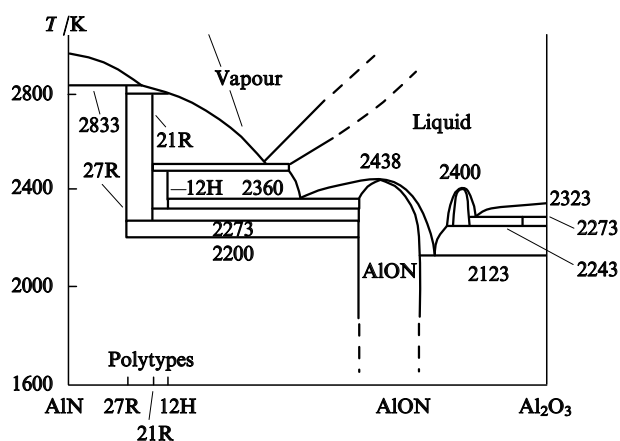


Figure 5. The AlN – Al_2O_3 phase diagram with identification of the regions corresponding to the formation of the AlN polytypes.¹²⁰

established by subsequent X-ray studies¹²² that all the new phases observed have a wurtzite type lattice and can be described in terms of Ramsdell's symbols as multilayer structures (polytypes based on the 2H AlN lattice) (Table 3). Depending on the number of layers (n) in the polytypes, their parameters c are described by the following equations:¹¹²

$$c_R = (n-3) \left(\frac{c}{2} \right)_{\text{AlN}} + 3(4.014),$$

$$c_H = (n-2) \left(\frac{c}{2} \right)_{\text{AlN}} + 2(4.014).$$

Table 3. Characteristics of the identified polytypes in the Si–Al–O–N system.

Polytype	M/X	<i>a</i> /Å	<i>c</i> /Å	<i>c</i> / <i>n</i> /Å	Ref.
8H	4/5	2.988	23.02	2.88	112
15R	5/6	3.010	41.81	2.79	112
12H	6/7	3.029	32.91	2.74	112
21R	7/8	3.048	57.19	2.72	112
27R	9/10	3.059	71.98	2.67	112
33R	11/12	—	86.46	2.62	122
24H	12/13	—	101.4	—	122
39R	13/14	—	—	—	122
2H ^δ (see ^a)	—	3.079	~5.30	2.65	112
2H	1/1	3.114	4.986	2.49	112

^a 2H^δ = solid solution of oxygen and silicon in 2H AlN.

A Si–Al–O–N phase diagram, in which the regions corresponding to the formation of AlN polytypes (or X-phases)¹⁰⁴ were identified, has also been put forward (Fig. 4).¹¹² This diagram, confirmed in a further study of the system, is nowadays widely known. According to the diagram, the polytypes are in the region with a high AlN content along a line corresponding to a constant cation/anion ratio. The polytypes described in the above study¹¹² were identified by electron microscopy¹²³ in a study of material having the initial composition Si₃N₄ + AlN + Al₂O₃ hot-pressed at 1600–1750 °C. Later in the course of similar studies of material obtained by sintering AlN + SiO₂, the 33R, 24H, and 39R polytypes were discovered and their characteristics were determined (Table 3).¹²² Overall, the composition of the polytypes in the Si–Al–O–N system is described by the general formula Al_{*x*} + *y*Si_{6–*y*}O_{*x*}N_{8–*x* + *y*}, where *x* = 4 and *y* = 2*n* (*n* is an integer varying from 0 to 10).

Polytypes have also been observed in the M–Si–Al–O–N systems. The 12H, 15R, 21R, and 20H polytypes were identified by X-ray diffraction in hot-pressed material based on the initial composition MgO + Al₂O₃ + Si₃N₄.¹¹² Subsequently the 12H, 15R, 7(21)R, and 8(16)H polytypes were found by electron microscopy in material of the same composition and it was established that they differ in the amounts of Mg–Al and Si–O.¹²⁴ According to the data of Kuang *et al.*,¹²⁴ the 12H polytype with the ratios Mg:Al:Si = 1:0.3:1.2 is formed in the Si–Al–O–N system in combination with MgO. It is also produced at 1400 °C and is stable up to the temperature of the appearance of the new phase.

The 15R polytype has been observed in the Si–Al–O–N system with lithium¹¹² and the 33R polytype was found in the same system with calcium.¹²⁵ Polytypes have been noted also in the system with yttrium. For example, the 15R and 8H polytypes were identified by Ekstrom *et al.*¹²⁶ at a sintering temperature less than 1800 °C, while the 27R polytype was identified by Topfer and Muller.¹²⁷

A characteristic feature of the polytype formation in the Y–Al–Si–O–N system must be pointed out.¹²⁸ The 27R polytype was formed in specimens having the initial composition AlN + SiO₂ at 1700–1800 °C; when Y₂O₃ was introduced into this composition, the amount of the polytype diminished. In the course of the subsequent annealing of a mixture of ground specimens having the first composition to which Y₂O₃ had been added, the content of the polytype fell, starting already at 1400 °C, whilst at higher temperatures it vanished altogether. This feature is due to the formation of oxygen-rich stable phases in the Al₂O₃–Y₂O₃ system above 1250 °C. This in fact induces the binding of the oxygen present in the initial AlN + SiO₂ system and also contained in specimens in which the 27R polytype is present after sintering.

d. Microstructural features of the formation of polytypes

The polytype formation in the Al–O–N and Si–Al–O–N systems is characterised by the following general features.

The formation of polytypes is observed in most cases above 1700 °C, although there have been reports of their appearance in the Si–Al–O–N system at 1400 °C¹²⁹ and 1600 °C.¹³⁰ Polytypes are formed in materials obtained by sintering porous pressed materials produced by the usual hot pressing and isostatic pressing procedures. In the treatment of materials at high pressures and temperatures (starting from 2 GPa at 1700–1800 °C), polytypes are not formed.

In the first stage, polytypes are always formed within the grains. At 1700–1800 °C, the polytypes are in most cases produced in the form of lamellar interlayers in the grains (Fig. 2), whilst at higher sintering temperatures individual grains with the same morphology are formed in the materials.⁸⁵ When highly disperse AlN powders, obtained by plasmachemical synthesis, are sintered, thin lamellar interlayers may be formed within the limits of the entire grain. In rare instances, a polytype with the same number of layers is formed within a single grain.¹¹⁵ A typical example is a mixture of polytypes with different numbers of layers combined with a solid solution of oxygen or of oxygen and silicon in AlN (2H^δ). In the lamellar interlayers, they are usually present in the form of blocks of different thickness grown together, coherently *via* the (0001) planes, *i.e.* they actually constitute a composite modulated structure. The electron microdiffraction patterns of sections of the (1120) type through the grains show a series of non-systematic point reflections in the 00/*l* and *h*0/*l* rows (Fig. 6). In the course of the recrystallisation growth of the grains, the polytypic composition along the length of both the MP interlayer and the individual grains having the same composition remains unchanged. All the variants of the development of the granular structure are presented in Fig. 3. In the course of the growth of the grains, the fraction of MP in the polycrystalline material increases as a result of the diffusional rearrangement, of the 2H phase in the MP within the migrating boundary. It is significant that in this instance the reverse transformation 2H → MP may also take place. Reversible grain → boundary polytypic transitions also occur in SiC-based materials.

An unusual instance of polytype formation has been noted¹³¹ in the Si₃N₄–SiC system to which Er₂O₃ and AlN had been added: the 21R polytype (SiAl₆O₂N₆) crystallises epitaxially on the basal surface of the 6H SiC plates.

There is no information about the regions of stability of the AlN polytypes in the Al–O–N and Si–Al–O–N systems. Data on the tentative regions in which three polytypes are located on the AlN–Al₂O₃ phase diagrams have been published in only one study (Fig. 5).¹²⁰ However, careful investigations on these lines have not been carried out. It has been established reliably that, as the oxygen content in the initial AlN decreases, the number of layers in the polytypes rises. The longest-period 51R polytype has now been identified: it has a 17-layer sequence repeated three times; its oxygen content is 6.6 at.%.¹¹⁸ The 165R polytype identified by Kurdymov *et al.*¹¹⁵ most probably consists of

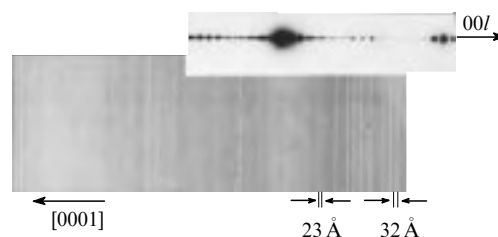


Figure 6. Interference pattern in the resolution of the 2H AlNO planes (0001) in an oxygen-enriched interlayer and an electron microdiffraction pattern [the (1120) section].

blocks of short-period structures, as is usually observed for SiC polytypes with a large number of layers (126R⁸⁰ and 201R⁸¹). It has also been established¹³² that at high pressures and temperatures (8–10 GPa and > 2200 °C) the multilayer polytypes in the AlN–O system are unstable: they undergo a transition to the 2H phase and the cubic aluminium oxynitride.

e. Models of the structure of AlN polytypes

A model of the structure of the wurtzite AlN polytypes was first proposed by Jack.¹¹² As in the case of the polytypes in the AlN–C system,^{91,101} it is based on the idea of the formation of multilayer structures from blocks of different chemical composition. The unit cell of each polytype contains n layers divided into blocks: two in the case of hexagonal and three in the case of rhombohedral symmetry. Each block consists in its turn of m layers. The number of layers in the hexagonal and rhombohedral polytypes is therefore represented as $n = 2m$ and $n = 3m$ respectively. One layer in each block contains an excess nonmetal atom, while the remaining layers are the basal (0001) 2H AlN layers. This means that the layer specified has the composition MX_2 , in contrast to the composition MX of the basic structure. On these grounds, the composition of the polytypes is described by the general formula M_mX_{m+1} , where m is an integer; we have the ratio $\text{M}/\text{X} < 1$. Hence a difference between the chemical compositions of the polytypes is evident.

The formation of layers having the composition MX_2 is determined by the local change in the coordination number of aluminium from four (characteristic of the 2H structure) to six and is induced by the dissolution of oxygen in AlN.¹¹² The change in the packing sequence in the AlN polytypes is attributed to the number and periodicity of the disposition of the MX_2 layers containing Al atoms with a coordination number of six. It has been suggested that the latter is determined by the appearance of packing defects in the aluminium sublattice of 2H AlN (the change in the AB, AB alternation of aluminium atoms to ABC, ABC), induced by the localisation of the nonmetal atoms and hence by the decrease in the distance between them.

In the subsequent structural studies, data were obtained confirming the proposed model of the structure of polytypes. It has been established by electron microscopy¹²³ that the change in the periodicity of the polytypes in the Si–Al–O–N system is determined by the presence of planar two-layer defects along the basal planes. On the basis of X-ray studies of two polytypes (8H and 15R), it was concluded that they contain 2H AlN layers distributed periodically in the basal planes and containing aluminium surrounded by six oxygen atoms (AlO_6).¹³³ The calculated images for the 12H and 15R polytypes, taking into account the regular alternation of the octahedrally coordinated aluminium atoms, corresponded to the images obtained by convergent beam electron diffraction.¹³⁴

On the basis of the ideas concerning multilayer structures in the AlN–C system developed by Jeffrey and Wu^{91,101} and Thompson's data,¹³³ Bartram and Slack¹⁰³ and Krishnan *et al.*¹¹⁶ suggested that the MX_2 layers in the polytypes of the Al–N–O system be regarded as $\alpha\text{-Al}_2\text{O}_3$ interlayers with a thickness equal to the parameter c of the morphological cell of corundum (the parameter c of this cell is equal to half the parameter c of the structural cell). In this model, the experimental and calculated values of c for the 20H and 27R polytypes agree well. The experimental values were respectively 53.10 and 72.24 Å. In the calculations, account was taken of the determinations of the interlayer distance and of the range of the known values of c for the morphological cell of Al_2O_3 . The following ranges of values of c (Å) were established: 50.92–53.58 for the 20H polytype and 68.77–72.76 for the 27R polytype.¹⁰³

In later studies, new data were obtained concerning the nature of the planar oxygen-containing MX_2 layers (O-defects) in the basal planes of AlN and a series of structural models of their formation were proposed. According to Hagege *et al.*,¹³⁵ such layers represent a packing defect containing an octahedrally

coordinated aluminium atom and arising with participation of vacancies generated on formation of the 2H AlN–O solid solution. It has been postulated¹³⁶ that the O-defects are anti-phase domain boundaries and their thickness in the direction of the [0001] axis of AlN is 1/2 or 1/3 of the $\alpha\text{-Al}_2\text{O}_3$ structural cell. Experimental studies established¹³⁷ that the defects are inversion domain boundaries (IDB) and that they contain lamellar formations enriched in oxygen.

According to the ideas of Harris *et al.*,¹³⁸ the logical sequence of the processes determining the formation of the O-defects is as follows. At an oxygen concentration less than 0.75 at.% in the 2H AlN–O solid solution the complexes $\text{V}_{\text{Al}} + \text{O}_{\text{N}}$, where V is a vacancy, are formed. It has been established experimentally that the formation of the complexes is accompanied by a decrease in the parameter c of 2H AlN and by the contraction of the lattice (Fig. 7). At higher oxygen concentrations, the mode of incorporation of oxygen into AlN changes (this is indicated by the restoration of the volume of the 2H lattice). It has been suggested¹³⁸ that in this case octahedral defects, the formation of which is accompanied by the annihilation of the aluminium vacancies, arise initially. A unit defect consists of a combination of an aluminium atom with six oxygen atoms. With increase in the oxygen concentration, such octahedral defects coalesce with formation of planar IDB, the regular disposition of which in the 2H lattice of AlN is in fact responsible for polytype formation.

A model of the structural rearrangement determining the formation of the O-defects has been proposed.¹³⁸ In this model, the development of a displacement process is postulated with a vector $\mathbf{R} = (1/3)\langle 10\bar{1}1 \rangle$, which may be split into two components: $\mathbf{R} = (1/3)\langle 10\bar{1}0 \rangle + (1/3)\langle 0001 \rangle$. This model has been confirmed.¹³⁹ In later studies, it was demonstrated experimentally that the vector of the displacement of the O-defect is $\mathbf{R} =$

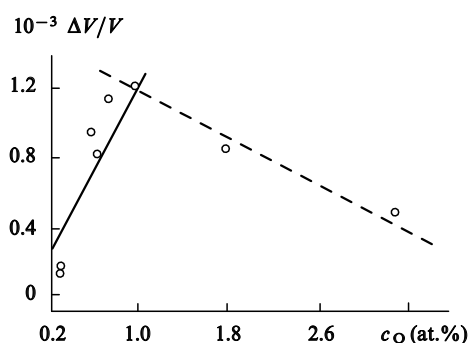


Figure 7. Variation of the volume ($\Delta V/V$) of the AlN unit cell with increase in the concentration of dissolved oxygen.¹³⁸

$(1/3)\langle 10\bar{1}0 \rangle + 0.387\langle 0001 \rangle$ and that this is close to the calculated value $\mathbf{R} = (1/3)\langle 10\bar{1}0 \rangle + 0.394\langle 0001 \rangle$.

The ideas¹³⁸ concerning the formation of planar IDB described are known as Youngman's model of the defect. This model has been confirmed:¹⁴⁰ the experimental oxygen content in the IDB (amounting to 6.0 ± 0.8 mass %) is close to the value calculated (5.7 mass %) in accordance with Youngman's model. We may note that the principal postulate of Youngman's model — the change in the structural state of oxygen in 2H AlN–O with increase in its concentration — has been confirmed also by the results of the study of the structure of this solution in thin films.¹⁴¹ It has been shown that the dissolution of oxygen in AlN with increase in concentration has three stages: I — complete dissolution; II — the formation of aluminium oxynitride; III — the formation of $\gamma\text{-Al}_2\text{O}_3$.

The nature of the periodic segregation of oxygen-containing basal layers in the 2H lattice and the mechanism of polytype formation in the 2H AlN–O solid solution were fully examined by the present authors in another communication.¹⁴² This was based

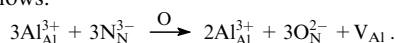
on the results of a detailed study by transmission electron microscopy in combination with microdiffraction of the evolution of structural transformations in the 2H AlN–O and 2H AlN–O–Si solid solutions, starting with the stage involving the appearance of unit basal packing defects in the grains and ending with the formation of lamellar grains made up of a mixture of multilayer AlN polytypes.

f. The model of the formation of polytypes

The formation of polytypes as a result of the generation of O-defects in the AlN basal layers is associated with two stages in the decomposition of the 2H AlN–O solid solution, which occurs above 1700 °C.¹⁴² According to experimental data, the first stage is the isostructural separation into layers, leading to the segregation in the single-crystal grains of oxygen-enriched lamellar interlayers, along the (0001) plane. A single plate is usually generated in the grain, intersecting it from boundary to boundary; its thickness in the [0001] direction is 0.5–1 µm (Fig. 2). The change in the oxygen concentration of the enriched lamellar interlayer in the [0001] direction is nonperiodic, because separation into layers occurs in each instant at a different concentration in the solid solution, *i.e.* a set of zones with different concentrations is formed in the interlayer.

The separation of the 2H AlN–O solid solution into layers occurs *via* the ascending diffusion mechanism (*i.e.* $\bar{D} < 0$, where $\bar{D}$ is the diffusion coefficient), caused by the sharp decrease in the energy of the basal packing defects within the grains of the 2H AlN–O solid solution.¹⁴² The decrease in energy is induced by the localisation of oxygen (Suzuki segregation) in the region of the packing defect. The occurrence of such segregations determines the appearance of a stress gradient as the driving force of ascending diffusion. The latter is due to the following causes.

Taking into account the conditions for isomorphous heterovalent substitution,⁸³ the 2H AlNO formation reaction is as follows:



The oxygen in such a solid solution exists in the form of the complexes $2\text{Al}_{\text{Al}}^{3+} + 3\text{O}_{\text{N}}^{2-} + \text{V}_{\text{Al}}$. The occurrence of oxygen segregations on the packing defect is associated with the migration of such complexes, *i.e.* with the simultaneous diffusion of aluminium along the cationic sublattice and of oxygen along the anionic sublattice, which means that it is associated with the constant appearance of a compressive stress (as a result of the presence of vacancies) in the vicinity of the packing defect. The magnitude of such stresses ε is proportional to the concentration of vacancies:¹⁴³

$$\varepsilon = \sum \beta_i N_i,$$

where β_i are deformation constants proportional to the difference between the ionic radii of the defects and the matrix and N_i is the concentration of point defects. Under the conditions of ascending diffusion under the influence of the stress gradient, atoms with a larger radius should tend to migrate into the stretched regions, while those with a smaller radius should tend to move into the compressed regions.¹⁴⁴ The latter (bearing in mind that $r_{\text{O}} < r_{\text{N}}$, where r represents the size of the atom) occurs in the case of 2H AlN–O and is responsible for the formation of oxygen-enriched layers along the planes containing the packing defect.

The second stage of the decomposition of the solid solution occurs in the oxygen-enriched interlayer produced on isomorphous separation into layers. It is determined by the sequence of structural transformations, the development of which is in fact responsible for the generation of basal O-defects and hence the formation of polytypes. These transformations occur in three stages.

1. The formation of oxygen clusters. The presence of such clusters is confirmed by the geometry of the reflections on the electron microdiffraction patterns from enriched interlayers (Fig. 8). The clusters are formed already in the process involving the separation of the solid solution into layers and consist of the

basal layers of AlN enriched to different extents by oxygen substituting the nitrogen atoms. It is believed that¹⁴⁵ the establishment of order in the system occurs as a result of the growth of some clusters and the disappearance of others. There is a definite correlation distance between the former clusters (which is due to the need to achieve the condition for the minimisation of their interaction energy). The minimisation condition determines also the form of the clusters, namely as Al–O basal layers. According to the ideas developed by Khachatryan,¹⁴⁶ in solid solutions with a negative anisotropy parameter, formations in the form of plates arranged in the direction of the minimum modulus of elasticity have the minimum elastic energy. For AlN, the anisotropy parameter is -0.07 . Evidently the cluster ordering process takes place, like the separation of the solid solution into layers, *via* the ascending diffusion mechanism. As noted above, a set of concentration zones are generated in the oxygen-enriched interlayers. Within the limits of each zone, clusters with a definite correlation distance are produced.

2. The formation of three-layer oxygen-containing defects from the clusters. This process is determined by the ordering of the vacancies in the AlN cationic lattice, inevitably accompanying the ordering of the clusters formed from associated species having the composition $(2\text{Al}_{\text{Al}}^{3+} + 3\text{O}_{\text{N}}^{2-} + \text{V}_{\text{Al}})$. One of the aluminium vacancies is formed after the substitution of three nitrogen atoms by oxygen, which means that the growth of clusters leads to the

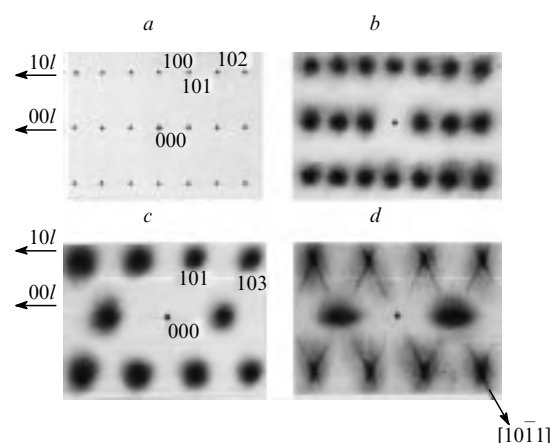


Figure 8. Schematic illustration of the electron microdiffraction pattern of the (1120) section through a grain of the initial 2H AlN–O solid solution (a) and of the interlayer formed as a result of layer formation (b–d); (b) and (c) nonordered cluster state; (d) state with directed stresses.

formation of three-layer defects in the (0001) planes — two oxygen-containing Al–O basal layers separated by a $\text{V}_{\text{Al}}\text{–O}$ layer. The segregation of such defects in the oxygen-enriched zone occurs with a periodicity specified by the motif in the disposition of the clusters. The presence of empty sublayers (V_{Al}) in the defects should lead to the appearance of directed stresses. This has in fact been confirmed by microdiffraction studies (Fig. 8 d).

3. The crystallographic shifts along the (0001) plane in three-layer defects. Such shifts lead to the exclusion of the vacancy sublayer and to a local rearrangement, of the 2H lattice in the defect into a fragment of the lattice of the $\alpha\text{-Al}_2\text{O}_3$ segregation phase. The shifts develop with a periodicity specified by the motif in the arrangement of the defects. The regular formation of layers of the segregation phase modulates the basic 2H structure to give a structure with a different phase composition and a different unit cell parameter c . Such structures actually represent polytypes.

The possible mechanism of the rearrangement of the three-layer defects to the Al–O segregation phase in the 2H AlN lattice is as follows: The bonds between the atoms in the three-layer defect differ from those in the 2H structure, because the appearance of even one vacancy V_{Al} on formation of the solid solution

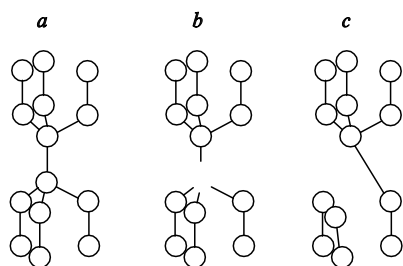


Figure 9. Schematic illustration of the single bond between diatomic layers in the 2H lattice with formation of aluminium vacancies [the (1120) section]; (a) normal unit; (b) formation of vacancies; (c) relaxation of the bond on formation of vacancies.

inevitably leads to the appearance of the O–O bond. This can be seen in Fig. 9, which represents a schematic arrangement of the atoms in a unit fragment of the 2H structure in the (1120) section. The appearance of a three-layer defect with a V_{Al} sublayer should lead to the formation of the O–O bond between the Al–O layers. The direction of this bond is parallel to the plane of the pyramid of the tetrahedron of the first kind (Fig. 10). The characteristic features of the structure of the electron microdiffraction pattern, of the (1120) sections of the interlayers containing the solid solution and multilayer AlN polytypes, namely the presence of diffuse rows in directions of the type $[10\bar{1}1]$ (Fig. 8d), may be regarded as confirmation of the formation of such a bond. Rows of this kind are known^{146, 147} to be a sign of the generation of directional stresses.

On formation of a continuous layer of vacancies, their collection into a loop is inevitable, which implies the formation of a chemical packing defect.¹⁴⁸ Such defects are characteristic of layered nonstoichiometric compounds, for example Sb_2Te_3 . In the three-layer defects in the AlN structure which we considered, the vacancies are located only in one sublayer of the diatomic layers. They then induce the appearance of directed stresses. Such stresses

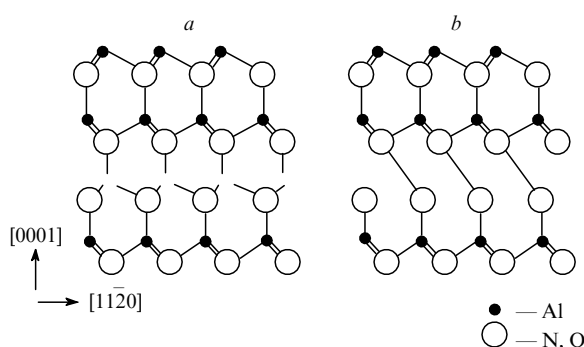


Figure 10. Schematic illustration of the formation of the O–O bond in a three-layer AlN defect formed following the ordering of the aluminium vacancies [the (1120) section]; (a) appearance of vacancies in the layer; (b) relaxation of the bond following the appearance of vacancies.

in the 2H lattice should promote a shift along the basal plane. According to the data of Funk and Sochel,¹⁴⁹ this type of shift occurs on disorientation (α) of the $[0001]$ axis and the directions in which the stresses act are in the range $0 < \alpha < 90^\circ$. In our case, the angle between the direction of type $[10\bar{1}1]$ and the $[0001]$ axis is 32° . The occurrence of such a shift promotes the elimination of the V_{Al} sublayer and may be classified in the development of the Wadsley crystallographic shift.¹⁵⁰

The elimination of the V_{Al} sublayer in the defect may be represented by two elementary steps involving the migrations of aluminium atoms under the influence of directed stresses

(Fig. 11a). The first involves the migration of the aluminium atoms from layer I (Al–O) to layer II (V_{Al} –O). Formally, this implies the formation of a packing defect, in the hexagonal close-packed aluminium sublattice, which is accompanied by a local change in the alternation of the atoms from AB AB... to ABC ABC.... The second step involves the migration of aluminium atoms in layer III (Al–O) over an interatomic distance. In this case, there is a shift in the (0001) plane. Such migrations are responsible for the change in the coordination number of aluminium from four to six and hence for the addition of oxygen atoms from layer II (V_{Al} –O). Formally, this can be represented as the combination of four tetrahedra (as elements of the wurtzite lattice) to form an octahedron which is an element of the structure of α - Al_2O_3 . Comparison of Fig. 11b with Fig. 12 shows that the disposition of aluminium and oxygen atoms in the lattice fragment, formed as a result, of the migrations indicated corresponds to their positions in two layers of the unit cell of α - Al_2O_3 .¹⁵¹ A distinctive feature of the structure of such a fragment compared with that of α - Al_2O_3 is that an aluminium atom from one layer is bound to five oxygen atoms and a nitrogen atom, *i.e.* it belongs simultaneously to the 2H lattice and the Al_2O_3 segregation phase. This also applies to the oxygen atom from the second layer because it is bound to an aluminium atom belonging to 2H AlN.

The thickness of two Al–O layers of the segregation phase is $c/4 = 3.24 \text{ \AA}$ (c is the cell parameter) (Fig. 12). We may note that, according to the data of Bartram and Slack,¹⁰³ the quantity $c/4$ may vary from 2.58 to 3.25 $\text{\AA}$. The estimation of the thickness of the layers of this phase in the 2H AlN lattice, taking into account, the distance between the aluminium and nitrogen atoms, yields 3.01 $\text{\AA}$ (the distance between diatomic layers in the direction of the c axis is 1.97 $\text{\AA}$, whilst that between the atoms in the diatomic layer is 0.52 $\text{\AA}$). This indicates the possibility of the formation of a fragment of the α - Al_2O_3 lattice structure in the form of two layers in the 2H AlN lattice. The segregation of AlO in the α -form is determined by the similarity of the ratios c/a in AlN and in this form ($c/a = 1.6$ in the former case and 1.58 in the latter) and also of the distances between the atoms in them: the distances between close unlike atoms are 1.97 and 1.86 $\text{\AA}$ in Al_2O_3 and 1.917 and 1.885 $\text{\AA}$ in AlN. The packing of the chains of oxygen atoms in the basal layers of the α - Al_2O_3 lattice is close to the packing of the nitrogen atoms in the AlN lattice. The principal difference between these structures is associated with the coordination number and also

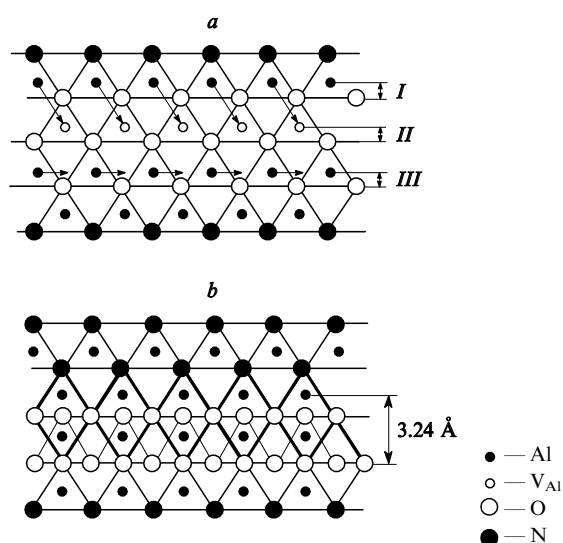


Figure 11. Schematic illustration of the migration of aluminium atoms in a three-layer defect on elimination of a sublayer of aluminium vacancies (a) and the disposition of the aluminium and oxygen atoms in the two-layer segregation generated after the elimination of the above sublayer (b) [the (1120) section].

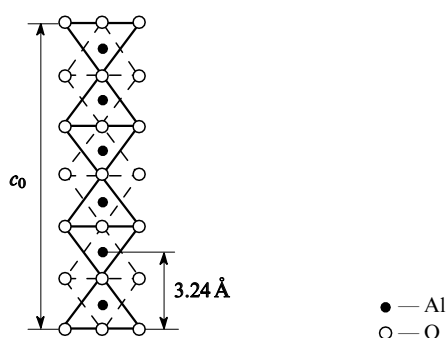


Figure 12. Schematic illustration of the disposition of aluminium and oxygen atoms in Al_2O_3 [the (1120) section].

with the disposition of the central aluminium atom: it has a coordination number of 6 and is located in an octahedral environment in an $\alpha\text{-Al}_2\text{O}_3$, whereas in AlN a coordination number of 4 is characteristic of this atom and the latter is located in a tetrahedral environment. Thus the rearrangement in the three-layer defect on development of the shift ensures a change in the location and hence in the coordination number of aluminium.

The lattice parameters of 2H AlN and $\alpha\text{-Al}_2\text{O}_3$ in the coupling plane differ appreciably ($a = 3.11$ Å for AlN and 4.748 Å for Al_2O_3), so that the following question arises inevitably: is the formation of $\alpha\text{-Al}_2\text{O}_3$ layers in the 2H AlN lattice possible? From a formal point of view, the noncorrespondence stress in their coupling plane, estimated from the relation

$$\sigma = \frac{E}{1 - \nu} \frac{a_{\text{Al}_2\text{O}_3} - a_{\text{AlN}}}{a_{\text{cp}}},$$

($E = 350$ GPa is Young's modulus and $\nu = 0.18$ is the Poisson coefficient) should be 178 GPa. This greatly exceeds the theoretical limiting strength for a $\mu/10$ shear (the modulus of shear is $\mu = 30$ ¹⁵²) and 137 GPa.¹⁵³ However, according to Khachaturyan's ideas,¹⁴⁶ in the case where a second phase is segregated in the solid solution in the form of thin plates for a small d/l ratio (d is the thickness and l the length of the plates), the interphase stresses should be extremely insignificant. In our case, this ratio is of the order of 10^{-4} . We may note that the deposition of AlN layers on $\alpha\text{-Al}_2\text{O}_3$ supports with epitaxial intergrowth along the basal planes has been observed by a number of investigators, for example by Dobrynin *et al.*¹⁰⁰

g. Calculation of the parameter c for the polytypes in the Al-N-O and Si-Al-N-O systems

According to modern ideas, the structural elements of the classical polytypes (SiC , ZnS , *etc.*) with hexagonal and rhombohedral symmetries consist respectively of two and three symmetrically disposed blocks with one structural packing defect. According to Oleinik and Shevchenko,¹⁴² in the AlN polytypes there should be for each block, not a packing defect, but a two-layer segregation of Al_2O_3 with a thickness $c/4$. The number of 2H AlN layers per structural cell of the polytype can be determined by subtracting from the total number of layers the number of two-layer Al_2O_3 fragments, which is four for polytypes with hexagonal symmetry and six for those with rhombohedral symmetry. For example, in a 20-layer hexagonal polytype containing four Al_2O_3 fragments (with a thickness $c/4$), there should be 16 2H AlN layers. The compositions (corresponding to the morphological cell, *i.e.* to one block) of the polytypes have been determined by means of this approach with the increase in the number of AlN layers in the formula unit from 1 to 15. The parameters c of these polytypes were calculated from the compositions and dimensions (the parameter d_{002}) of unit AlN and Al_2O_3 layers in the direction of the $[0001]$ axis. This quantity is 2.49 Å for AlN and is equal to the

Table 4. Characteristics of the polytypes in the AlN-Al-O system.

Poly-type ^a	M/X	Composition	No. of layers		$c/\text{Å}$	
			AlN	Al_2O_3	I ¹⁴²	II ¹¹⁶
9R	3/4	$\text{Al}_3\text{O}_3\text{N}$, $\text{AlN} \cdot \text{Al}_2\text{O}_3$	3	6	26.91	—
8H	4/5	$\text{Al}_4\text{O}_3\text{N}_2$, $2\text{AlN} \cdot \text{Al}_2\text{O}_3$	4	4	22.92	—
15R	5/6	$\text{Al}_5\text{O}_3\text{N}_3$, $3\text{AlN} \cdot \text{Al}_2\text{O}_3$	9	6	41.85	—
12H	6/7	$\text{Al}_6\text{O}_3\text{N}_4$, $4\text{AlN} \cdot \text{Al}_2\text{O}_3$	8	4	32.88	—
21R	7/8	$\text{Al}_7\text{O}_3\text{N}_5$, $5\text{AlN} \cdot \text{Al}_2\text{O}_3$	15	6	56.81	—
16H	8/9	$\text{Al}_8\text{O}_3\text{N}_6$, $6\text{AlN} \cdot \text{Al}_2\text{O}_3$	12	4	42.84	40.7
27R	9/10	$\text{Al}_9\text{O}_3\text{N}_7$, $7\text{AlN} \cdot \text{Al}_2\text{O}_3$	21	6	71.75	72.0
20H	10/11	$\text{Al}_{10}\text{O}_3\text{N}_8$, $8\text{AlN} \cdot \text{Al}_2\text{O}_3$	16	4	52.8	53.1 ^b
33R	11/12	$\text{Al}_{11}\text{O}_3\text{N}_9$, $9\text{AlN} \cdot \text{Al}_2\text{O}_3$	27	6	86.89	—
24H	12/13	$\text{Al}_{12}\text{O}_3\text{N}_{10}$, $10\text{AlN} \cdot \text{Al}_2\text{O}_3$	20	4	62.76	—
39R	13/14	$\text{Al}_{13}\text{O}_3\text{N}_{11}$, $11\text{AlN} \cdot \text{Al}_2\text{O}_3$	33	6	101.61	—
28H	14/15	$\text{Al}_{14}\text{O}_3\text{N}_{12}$, $12\text{AlN} \cdot \text{Al}_2\text{O}_3$	24	4	70.72	—
45R	15/16	$\text{Al}_{15}\text{O}_3\text{N}_{13}$, $13\text{AlN} \cdot \text{Al}_2\text{O}_3$	39	6	116.55	—
32H	16/17	$\text{Al}_{16}\text{O}_3\text{N}_{14}$, $14\text{AlN} \cdot \text{Al}_2\text{O}_3$	28	4	82.68	82.82
51R	17/18	$\text{Al}_{17}\text{O}_3\text{N}_{15}$, $15\text{AlN} \cdot \text{Al}_2\text{O}_3$	45	6	131.49	—

Note. The following designation have been adopted: I — calculations; II — experiment. ^a Polytypes the designation of which are printed bold were established experimentally, whilst the remaining ones are hypothetical. ^b Data of Bartam and Slack.¹⁰³

thickness of the two-layer lattice fragment, *i.e.* to 3.24 Å, for Al_2O_3 . The above characteristics of the polytypes are presented in Table 4. Evidently all known polytypes fit within the above sequence. The calculated values of c agree well with the experimental results for certain polytypes.

The polytypes in the $\text{Al}_2\text{O}_3\text{-AlN}$ system can be represented by the general formula $z\text{AlN} \cdot \text{Al}_2\text{O}_3$, where z is any integer. The number of layers in the polytypes with rhombohedral (n_R) and hexagonal (n_H) symmetries in the sequence deduced above (Table 4) is described by the following relations:

$$n_R = 9 + 6n,$$

$$n_H = 8 + 4n,$$

where n is an integer: $0 < n < 7$ in the former case and $0 < n < 6$ in the latter.

The proposed mechanism¹⁴² of polytype formation in the 2H AlN-O solid solution can operate in the four-component Al-N-Si-O solid solution. The following considerations lead to this conclusion.

When the above solid solution is produced, the positively charged centres ($\text{Si}^{4+} - \text{N}^{3-}$) and ($\text{Al}^{3+} - \text{O}^{2-}$) are generated. The electroneutrality of the lattice can be ensured, as in the case of the 2H AlN-O solid solution, by the formation of the associated species $\text{Si}^{4+} + \text{Al}^{3+} + 2\text{O}^{2-} + \text{N}^{3-} + \text{V}_{\text{Al}}$. The associated species of the system under consideration include two cations and three anions. This suggests that a similar segregation based on the clusters occurs in the system with silicon but differs in the formula

composition, which corresponds to the composition of the electrically neutral complexes, *i.e.* AlSiNO_2 . The latter is a sialone phase. The existence of such phases with the composition MSiNO_2 ($M = \text{Ce, La, Y}$) has been reported,¹⁵⁴ but their structure has not been investigated. On the basis of conditions for isomorphous substitution in the Si–Al–O–N system, this phase can be represented as a solid solution of silicon and nitrogen in $\alpha\text{-Al}_2\text{O}_3$. Consequently the thickness of the two-layer segregation with the composition AlNSiO_2 in the polytypes based on 2H AlN-SiO should be close to 3.24 Å, which is characteristic of the segregations in the 2H AlNO solid solution.

The thickness of the two-layer segregation in the polytypes of the AlN-SiO_2 system can be calculated with the aid of experimental parameters c for the known polytypes in this system using the following relation:¹¹²

$$(d_{002})_{\text{AlNSiO}_2} = \frac{c - v(d_{002})_{\text{AlN}}}{w},$$

where v and w are the numbers of AlN and AlNSiO_2 layers per unit cell. The calculated thickness of the AlNSiO_2 segregation is ~ 3.25 Å, *i.e.* is close to the thickness of the $\alpha\text{-Al}_2\text{O}_3$ fragment in the polytypes of the $\text{AlN-Al}_2\text{O}_3$ system.

The formula compositions and the parameters c of various polytypes in the AlN-SiO_2 system have been calculated taking into account the composition and thickness of the segregation (3.25 Å) (Table 5). Evidently the calculated and experimental parameters are identical for the known polytypes.

The compositions of the 15R and 12H polytypes were identified as $\text{Al}_4\text{O}_2\text{N}_4\text{Si}$ and $\text{Al}_5\text{O}_2\text{N}_5\text{Si}$ respectively with the aid of X-ray dispersion-energetic spectroscopy and electron loss spectroscopy.¹⁵⁵ Overall, the polytypes in the AlN-SiO_2 system can be described by the general formula $\text{Al}_{x+y}\text{Si}_{6-x}\text{O}_x\text{N}_{8-x+y}$, where $x = 4$ and $y = 2n$ (n is an integer varying from 0 to 10).

Table 5. Characteristics of the polytypes in the AlN-SiO_2 system.

Polytype	M/X	Composition	x	y	No. of layers		$c/\text{Å}$	
					see ^a	see ^b	I	II
9R ^c	3/4	$\text{Al}_2\text{SiN}_2\text{O}_2$, $\text{AlN}(\text{AlNSiO}_2)$	4	0	3	6	26.97	—
8H	4/5	$\text{Al}_3\text{SiN}_3\text{O}_2$, $2\text{AlN}(\text{AlNSiO}_2)$	4	2	4	4	22.96	23.02
15R	5/6	$\text{Al}_4\text{SiN}_4\text{O}_2$, $3\text{AlN}(\text{AlNSiO}_2)$	4	4	9	6	41.91	41.81
12H	6/7	$\text{Al}_5\text{SiN}_5\text{O}_2$, $4\text{AlN}(\text{AlNSiO}_2)$	4	6	8	4	32.92	32.91
21R	7/8	$\text{Al}_6\text{SiN}_6\text{O}_2$, $5\text{AlN}(\text{AlNSiO}_2)$	4	8	15	6	56.85	57.19
16H ^d	8/9	$\text{Al}_7\text{SiN}_7\text{O}_2$, $6\text{AlN}(\text{AlNSiO}_2)$	4	10	12	4	42.88	—
27R	9/10	$\text{Al}_8\text{SiN}_8\text{O}_2$, $7\text{AlN}(\text{AlNSiO}_2)$	4	12	21	6	71.79	71.98
20H ^d	10/11	$\text{Al}_9\text{SiN}_9\text{O}_2$, $8\text{AlN}(\text{AlNSiO}_2)$	4	14	16	4	52.84	—
33R	11/12	$\text{Al}_{10}\text{SiN}_{10}\text{O}_2$, $9\text{AlN}(\text{AlNSiO}_2)$	4	16	27	6	86.73	86.46
24H	12/13	$\text{Al}_{11}\text{SiN}_{11}\text{O}_2$, $10\text{AlN}(\text{AlNSiO}_2)$	4	18	20	4	62.80	—
39R	13/14	$\text{Al}_{12}\text{SiN}_{12}\text{O}_2$, $11\text{AlN}(\text{AlNSiO}_2)$	4	20	33	6	101.67	101.4

Note. The following designations have been adopted: I — calculation,¹⁴² II — experiment.^{112, 122} ^aNo. of AlN layers. ^bNo. of AlNSiO_2 layers. ^cHypothetical polytype. ^dPolytype identified in the Mg-Si-Al-O-N system.¹¹⁹

h. The role of oxygen in AlN polytype formation

The scheme for the structural transformations in 2H AlN-O examined above suggests that the polytype formation in AlN is determined by the regular endotaxy of the Al_2O_3 layers in the 2H matrix in the direction $[0001]$, while the polytypes are intergrowth microstructures. The latter are characterised by the fact that the intergrowth phases have a common cationic sublattice, but in one of them the sublattice atoms are located in tetrahedral vacancies (AlN), whilst in the other they are in octahedral vacancies (Al_2O_3). Overall, the structural changes in the 2H AlN-O solid solution, which determine polytype formation, are analogous to the changes characteristic of the ageing of solid alloys. The latter is accompanied by a stage of separation into layers and the subsequent stage involving the local formation of the lattice of the segregation phase.¹⁵⁶ Different AlN polytypes can be represented by a series of consecutive stoichiometric ordered phases.

The mechanism of the AlN polytype formation described for systems with only oxygen and for systems with a combination of oxygen and nitrogen makes it possible to account for the exceptional role of oxygen. The key structural transformations, determining the formation of the AlN polytypes (the separation of the solid solution into layers with formation of an oxygen-enriched zone, the formation of three-layer oxygen-containing defects as concentration inhomogeneities with an ordered arrangement in such zones) are associated with the development of ascending diffusion. In the case of the 2H AlNO solid solution, the latter may occur only as a result of the stress gradients generated by the aluminium vacancies. The ordered vacancies V_{Al} , disposed in the O-V_{Al} layer, are also 'responsible' for the shear as the final stage of polytype formation.

Thus the polytype formation in AlN is a vacancy-stimulated process, *i.e.* it occurs only in the presence of vacancies in the system. The energy of formation of structural vacancies in AlN is high (according to Cormack,¹⁵⁷ it amounts to 62.998 eV for V_{Al} and 52.108 eV for V_{N}) and they are therefore manifested in the formation of solid solutions. Among chemical elements the dissolution of which in AlN with formation of vacancies is possible, the nitrogen–oxygen, aluminium–silicon, and nitrogen–carbon pairs satisfy best the isomorphous substitution conditions (isoelectronic structure, chemical indifference, similarity of the atomic radii, and similarity of the electronegativities).

There are few experimental data on the formation of solid solutions in 2H AlN . It has been established¹⁵⁸ that oxygen may substitute up to 1/3 of the nitrogen atoms in thin AlN films; when the degree of substitution is high and $T = 800 - 1000$ °C, amorphisation takes place. The AlN in films may be saturated with oxygen up to the compositions AlN_xO_y and $\gamma\text{-Al}_2\text{O}_3$.¹⁴¹ The dissolution of oxygen in AlN up to 1 at.% induces compression of the lattice,¹¹⁸ whilst at higher concentrations the lattice is restored (Fig. 7). The fact that the replacement of three nitrogen atoms by oxygen leads to the formation of V_{Al} is generally recognised. A positive energy of mixing is characteristic of the 2H AlNO solid solutions. This is confirmed by the heating thermogram for a highly disperse AlN powder containing ~ 3 mass% of oxygen.⁸⁵ Analysis of the thermogram indicates the presence of endothermic effects on heating up to 1450 °C, which suggest a positive deviation of the solid solution from the ideal state, *i.e.* from Raoult's law.¹⁵⁹ The latter actually determines its separation into layers, *i.e.* a solid-state structural rearrangement with formation of two solid solutions — enriched and depleted in the dissolved element. The segregation of the first solution in the form of a plate bounded by the (0001) surfaces is induced by a heterogeneous mechanism of separation into layers (with participation of basal packing defects).

The solubility of silicon in AlN as an individual element has not been determined. An attempt has been made¹⁶⁰ to investigate this process in AlN films. It was established that, with increase in silicon concentration in AlN , the unit cell parameter a diminishes, whilst c initially increases and then falls. On the basis of these data,

it has been suggested that oxygen is present in AlN films together with silicon.

The dissolution of SiO₂ in AlN has been demonstrated reliably. As in the case of the AlN–O system, this process takes place with formation of V_{Al}:



With increase in the SiO₂ concentration in the AlN–SiO₂ system, the parameter c of AlN diminishes (Fig. 13).¹⁶¹

Taking into account the literature data,^{118, 160, 161} one may assume that the simultaneous dissolution of oxygen and silicon in AlN should be regarded as a result of the mutual influence of the donor (Si) and acceptor (O) impurities. The replacement of aluminium by silicon promotes the appearance of an electron in the system and this should facilitate the dissolution of the acceptor impurity.¹⁶² It is seen from the reaction, presented above, involv-

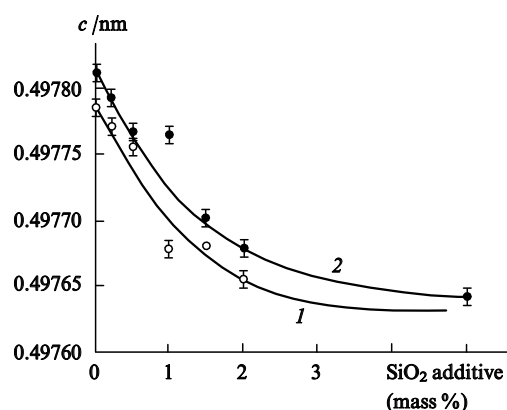


Figure 13. Variation of the parameter c of the AlN unit cell with increase in the concentration of SiO₂ in polycrystalline specimens. Sintering medium: (1) air; (2) nitrogen.

ing the dissolution of SiO₂ in AlN, that V_{Al} is formed on substitution of two nitrogen atoms by oxygen and not on substitution of three atoms as happens on dissolution of oxygen alone. Thus silicon plays the role of the catalyst, in the dissolution of oxygen in AlN.

There is no information about the dissolution of carbon in AlN. Presumably, in conformity with the conditions for isomorphous substitution,⁸³ carbon substitutes nitrogen in AlN with formation of vacancies in the anionic sublattice (V_N). The structural transformations in the 2H AlN–C solid solution may occur in accordance with the scheme proposed for the 2H AlNO solid solution subject to the difference that their development is controlled by anionic vacancies. Data on polytype formation in the BeSiN₂–Be₃N₂ system may serve as confirmation of this hypothesis. In the above system, the vacancies arise in the anionic sublattice of the BeSiN₂ wurtzite phase, on the basis of which polytypes actually appear as a result of the periodic segregation of Be₃N₂ layers in the direction of the [0001] axis of the 2H lattice.¹⁶³

On simultaneous dissolution of oxygen and carbon in AlN, polytypes are not formed (for example in the AlN–Al₂O₃C system).¹⁶⁴ On dissolution, there is in this instance a possibility of the formation of oppositely charged centres, (Al³⁺ – C^{4–}) and (Al³⁺ – O^{2–}), which leads to charge compensation in the AlN lattice without the formation of vacancies. Furthermore, the polarisability of carbon anions is greater than that of oxygen (according to Slabough and Parsons,¹⁶⁵ the polarisability is directly proportional to the ionic volume and the radii of the carbon and oxygen ions are 2.6 and 1.35 Å respectively), *i.e.* carbon shows a greater tendency towards the formation of chemical compounds. This has been confirmed by data on the formation in the Al–N–O–C system of the compound Al₄O₄C with a melting

point < 1700 °C, *i.e.* below the temperature at which the 2H AlNO solid solution separates into layers (the necessary stage of the structural rearrangement in polytype formation). It has been established¹⁶⁶ that, in the joint presence of oxygen and carbon in AlN, the phase with the composition (Al₂O₃)·AlN may be formed. This composition was regarded¹⁶⁷ as a solid solution of AlN in Al₂O₃. In the same study, it was established that, for an AlN content corresponding to 40 mol % of nitrogen, the ordered Al₁₀O₃C₉N₄ phase is segregated in the solid solution.

The mechanism of polytype formation in AlN on dissolution of oxygen in the latter, described above, is supported by the following known experimental facts obtained in the study of AlN-based materials.

1. The decrease in the concentration of vacancies when the oxygen content dissolved in AlN is > 1 at.% (*i.e.* in the range of compositions where polytypes can already be formed).¹¹⁸ The critical nature of this oxygen concentration, which exhibits a radical influence on the AlN structure, has also been confirmed by the analysis of the Raman spectra of the 2H AlN–O solid solution.¹⁶⁸

2. The fact that the short-period polytypes are incommensurate, which may be attributed to the high concentration of Al₂O₃ layers.¹⁶⁹

3. The presence of lamellar O-containing segregations in planar AlN defects.¹³⁷

4. The absence of polytype formation in the 2H AlN–O solid solution and the decomposition of polytypes at a high pressure with the appearance of 2H AlN and aluminium oxynitride.¹³² This can be explained by the thermodynamics of the development of structural rearrangements at a high pressure: the rearrangements involving the formation of vacancies (as happens necessarily on dissolution of oxygen in AlN) are unfavourable, whilst the rearrangements involving the disappearance of vacancies (which happens on formation of aluminium oxynitride as a result of the dissolution of nitrogen in Al₂O₃) are actually favourable.

5. The agreement between the calculated compositions of the 12H and 15R polytypes in the Si–Al–O–N system and the experimental compositions established by Bando *et al.*¹⁵⁵

6. The absence of polytype formation in 2H AlN–O in the presence of impurities ensuring the charge compensation of the lattice following the replacement of nitrogen by oxygen (BeO, SiC).^{170, 171}

7. The presence of the Al₂O₃ band in the luminescence spectrum of AlN containing up to 2.8% of oxygen.¹⁷²

8. The presence of the Al₂O₃ band in the 51R spectrum of a lamellar AlN crystal made up of multilayer polytypes.¹⁷³

9. The agreement between data on the content of oxygen in the 51R polytype quoted by Youngman and Harris¹¹⁸ and Oleinik and Shevchenko¹⁴² (6.6 at.% and 8.5 at.% respectively).

6. Beryllium siliconitride and beryllium oxide

Two series of polytypes exist in the Be–Si–O–N system. On the phase diagram, they are located along the line corresponding to the constant cation/anion ratio in the BeSiN₂–BeO–Be₃N₂ range of compositions. The available information about these polytypes (based on the data of Shaw and Thomas¹⁶³) is presented in a generalised form in Tables 6 and 7. One series of polytypes are formed on the basis of the 2H BeSiN lattice along the BeSiN₂–Be₃N₂ connecting line, whilst another series are formed on the basis of 2H BeO along the BeO–Be₃N₂ connecting line.

The polytypes in the system considered have been observed as individual ternary phases (Be–Si–N and Be–O–N) by Heseby *et al.*¹⁷⁴ in a study of the Si₃N₄–SiO₂–BeO–Be₃N₂ quasi-ternary system along an isothermal section (1700 °C). These phases were identified by X-ray diffraction also in the Si₃N₄–Be₃N₂–BeO system. They were represented as multilayer structures with different M/X ratios and have been described in terms of Ramsdell's symbols.^{175, 176} Thompson and Gauchler¹⁷⁶ constructed the Be–Si–O–N phase diagram on the basis of the results of their own studies and those of Heseby *et al.*¹⁷⁴ The regions where

Table 6. The compositions and the parameters c of the unit cell for polytypes of the BeSiN_2 – Be_3N_2 series.

Poly-type	M/X	No. of layer		Composition		$c/\text{\AA}$	
		see ^a	see ^b	I	II ¹⁷⁴	I	II ¹⁷⁵
4H Be_3N_2 ^c	3:2	4	—	Be_3N_2	Be_3N_2	9.693	9.693
9R	4:3	6	3	Be_7SiN_6	—	12.567	—
8H	5:4	4	4	Be_4SiN_4	Be_4SiN_4	19.064	19.22
15R	6:5	6	9	$\text{Be}_9\text{Si}_3\text{N}_{10}$	$\text{Be}_9\text{Si}_3\text{N}_{10}$	35.625	36.32
12H	7:6	4	8	$\text{Be}_5\text{Si}_2\text{N}_6$	$\text{Be}_5\text{Si}_2\text{N}_6$	28.44	29.10
21R	8:7	6	15	$\text{Be}_{11}\text{Si}_5\text{N}_{14}$	$\text{Be}_{11}\text{Si}_5\text{N}_{14}$	49.68	50.98
16H ^d	9:8	4	12	$\text{Be}_6\text{Si}_3\text{N}_8$	—	37.81	—
27R ^d	10:9	6	21	$\text{Be}_{13}\text{Si}_7\text{N}_{18}$	$\text{Be}_{13}\text{Si}_7\text{N}_{18}$	63.74	65.11
BeSiN_2 ^e	1:1	—	2	BeSiN_2	BeSiN_2	4.69	4.69

Note. The following designations have been adopted: I — calculation; II — experiment. ^a The number of Be_3N_2 layer. ^b The number of BeSiN_2 layer. ^c The hexagonal phase ($a = 2.842$, $c = 9.706$ Å), the distance between the close-packed layers is 2.423 Å. ^d Hypothetical polytype. ^e Orthorhombic ordered wurtzite structure ($a = 4.977$, $b = 5.747$, $c = 4.674$ Å), the distance between the close-packed layers is 2.343 Å.

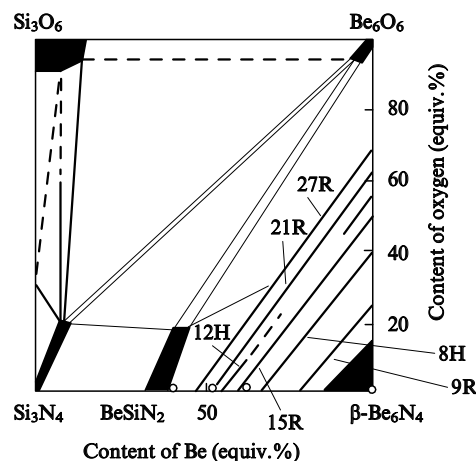
Table 7. The compositions and the parameters c of the unit cell for polytypes of the BeO – Be_3N_2 series.

Poly-type	M/X	No. of layer		Composition		$c/\text{\AA}$	
		see ^a	see ^b	I	II ¹⁷⁴	I	II ¹⁷⁵
4H Be_3N_2 ^c	3:2	4	—	Be_3N_2	Be_3N_2	9.693	9.693
9R	4:3	6	3	Be_4ON_2	—	21.099	—
8H	5:4	4	4	$\text{Be}_5\text{O}_2\text{N}_2$	—	18.44	—
15R	6:5	6	9	$\text{Be}_6\text{O}_3\text{N}_2$	$\text{Be}_6\text{O}_3\text{N}_2$	34.22	34.58
12H	7:6	4	8	$\text{Be}_7\text{O}_4\text{N}_2$	—	17.19	—
21R	8:7	6	15	$\text{Be}_8\text{O}_5\text{N}_2$	$\text{Be}_8\text{O}_5\text{N}_2$	47.34	47.87
16H ^d	9:8	4	12	$\text{Be}_9\text{O}_6\text{N}_2$	—	35.94	—
27R ^d	10:9	6	21	$\text{Be}_{10}\text{O}_7\text{N}_2$	—	60.47	61.05
BeO ^e	1:1	—	2	BeO	BeO	4.38	4.38

Note. The following designations have been adopted: I — calculation; II — experiment. ^a The number of the Be_3N_2 layer. ^b The number of the Be_2O_2 layer. ^c The distance between the close-packed layers is 2.423 Å. ^d Hypothetical polytype. ^e The distance between the close-packed layers is 2.187 Å.

various polytypes are located were identified on the diagram (Fig. 14).

Clarke *et al.*¹⁷⁷ proposed for the first time a model of the structure of polytypes in the system under consideration. It is based on the motif of a regular defective wurtzite structure with the general formula $M_m + 1X_m$, where the minimum value of m ($m = 2$) corresponds to the Be_3N_2 structure. According to the authors,¹⁷⁷ the formation of polytypes is determined by the periodic incorporation of the M_2X layers into the MX blocks of the basic 2H structure of BeSiN_2 . This model has been confirmed by electron microscope studies on polycrystalline specimens containing the polytypes in the BeSiN_2 – Be_3N_2 system: Shaw and Thomas^{163,178} observed regularly arranged planar defects in the structure of the 2H BeSiN_2 -based polytypes. It was suggested¹⁶³ that this structure of the polytypes is due to the formation of defects having a structure and composition different from those of the basic wurtzite structure. Each defect consists of two cubically packed Be_3N_2 layers forming a hexagonal unit cell. These defects promote the transformation of the 2H structure into a set of structures with different phase compositions and volumes of the

**Figure 14.** The isothermal section through the Be–Si–O–N phase diagram at 1780 °C.¹⁷⁶

unit cells. The size of the unit cell is determined by the distance between the defects. According to Shaw and Thomas,¹⁶³ the appearance of Be_3N_2 layers is induced by the ordering of the vacancies in the nonmetallic BeSiN_2 sublattice and the subsequent exclusion of the resulting sub-layers of vacancies as a result of a crystallographic shift along the (0001) direction. Dislocations with a Burgers vector of the type $1/6\langle 20\bar{3} \rangle$ were identified in the BeSiN_2 structure. The shift probably occurs with the aid of these dislocations.¹⁶³ The development of such a shift is responsible for the appearance of the beryllium-enriched planar defects corresponding to the Be_3N_2 composition.

On the basis of the postulates concerning the structure of the polytypes in the BeSiN_2 – Be_3N_2 system described above and having adopted a similar model for the structure of the polytypes in the BeO – Be_3N_2 system, Shaw and Thomas¹⁶³ determined the tentative compositions of a series of polytypes in these systems and calculated the dimensions of the unit cells in the direction of the c axis (Table 7). Evidently these data agree with the experimental results for the polytypes in the Be–O–N system.

7. Boron nitride

As in carbon, polytypes based on three modifications are formed in boron nitride: graphite-like, wurtzite, and sphalerite. The polytypes based on the first modification are formed as intermediate structures in the 2H BN $\rightarrow$ graphite-like BN transition. This transition, which occurs *via* the mechanism of the explosive martensite transformation, has been observed directly in the study of the 2H BN particles by means of a transmission electron microscope. It involves the type of transformation in which a particle of the initial phase is converted into a particle consisting of the graphite-like BN and the polytypes based on it.¹⁷⁹ On sintering polycrystalline 2H BN specimens, this transformation occurs on the surfaces of the layered region.¹⁸⁰

The 2H BN $\rightarrow$ MP + 3C BN transition occurs at high temperatures and pressures. It has been established by electron microscope studies¹⁸¹ that at $P = 5$ GPa the transition begins already at 1200 °C and takes place intragranularly *via* a shift mechanism with the aid of Shockley particle dislocations and with a Burgers vector of the type $1/3a[10\bar{1}0]$. As a rule, the transformation results in the formation of a mixture of polytypes. In rare instances, only one polytype is obtained. The 15R polytype has been identified¹⁸² on the basis of 2H BN, whilst in another study¹⁸³ the 4H polytype was identified. In the primary recrystallisation stage, which occurs in heterophase crystals (2H BN + 3C BN + MP), the intergranular transformation $2\text{H} \rightarrow 3\text{C}$, due to the migration of the interface, also occurs on sintering polycrystalline materials at high pressures.⁸⁶

As in the case of the dense cubic phase of carbon (diamond), the 3C BN-based polytypes are formed under the conditions of deformation at high pressures and temperatures. Their formation is associated with micro-twinning (the formation of thin high-density twinned crystals) in 3C BN crystals *via* a single system of planes of the type {111}.³³

8. Transition metal carbides and nitrides

The formation of multilayer structures is also characteristic of nonstoichiometric Group IV–VI transition metal carbides and nitrides of the type of interstitial phases. Taking into account the crystal geometry and the chemical composition of the interstitial phases (mainly carbides), a series of hypothetical monophase compounds as well as the mechanism of their formation, have been proposed.¹⁸⁴ It was postulated that these phases are formed as a result of the ordered alternation of hexagonal and cubic layers. They were designated in term of Jagodzinski's and Ramsdell's symbols (Table 8).

Many of the postulated phases (including those in the M–N–C system) were identified.^{19, 185, 186} The relation between the composition and the number of layers in polytypic structures has been found for certain carbides MC_y (M = V, Nb, and Ta):¹⁸⁴

$$y = 1 \quad 5/6 \quad 4/5 \quad 3/4 \quad 2/3 \quad 3/5 \quad 1/2$$

Table 8. The multilayer structures in the interstitial phase type transition metal carbides and nitrides.¹⁸⁴

Phase	Maximum content of non-metal (at.%)	Types and space groups of the possible types of packing
M ₂ X	33.3	<i>h</i> (2H); <i>hc</i> (4H); <i>h₃c</i> (8H); <i>h₅c</i> (12H'); <i>h₃chc</i> (6H')
M ₅ C ₃	37.5	<i>h₃c₂</i> (10H); <i>h₂chc</i> (10H); <i>h₄c</i> (15R); <i>hc₂hc</i> (15R)
M ₃ X ₂	40.0	<i>hc₂</i> (6H); <i>h₂c</i> (9R); <i>h₃c₃</i> (12H); <i>h₂chc₂</i> (12H); <i>h₄c₂</i> (18R); <i>hc₂hc</i> (18R); <i>h₂c₂hc</i> (12H)
M ₄ X ₃	42.8	<i>hc₃</i> (8H); <i>h₂c₂</i> (12R)
M ₅ X ₄	44.4	<i>h₂c₃</i> (5T); <i>hc₄</i> (10H)
M ₆ C ₅	45.5	<i>hc₅</i> (12H); <i>h₂c₄</i> (18R)
MC	50.0	<i>c</i> (3C)

Note. The following designations have been adopted for the space groups: H = *P6₃/mmc*, *D_{6h}⁴*; T = *P3m1*, *D_{3d}³*; H' = *P6m2*, *D_{3h}²*; C = *Fm3m*, *O_h⁵*; R = *R3m*, *D_{3d}⁵*; *h* and *c* = layers with hexagonal and cubic types of packing respectively.

Structure 3C(∞) (51)₃ 41 (31)₃ (21)₃ (32)₃ 2H(11)

Monophase ordered compounds are usually formed in the synthesis in the region of the coupling boundary between monocarbides with a hexagonal close-packed lattice and hemicarbides with a face-centred cubic lattice (this applies also to nitrides)^{185, 186} or during the ordering process.¹⁹ In most cases, these compounds are referred to as superstructures. A characteristic feature of the microstructures of many of them, namely the one-dimensional microdomain structure, has been established experimentally: for example, in V₆C₅,¹⁸⁷ Ta₆C₅,¹⁸⁸ Ti₃N_{2–x},¹⁸⁹ and certain vanadium, niobium, and tantalum carbides.¹⁸⁵

Two models of the ordering in carbides and nitrides of the type of interstitial phases are now known. One of the models takes into account the nonstoichiometry of these substances, namely the presence of vacancies in the nonmetallic lattice. A decisive role in the formation of the ordered state (*i.e.* in the appearance of superstructures) is attributed to the development of the process involving the ordering of the structural vacancies and the N and C atoms in the nonmetallic sublattice.¹⁹ The initial phases are in

essence interstitial solid solutions (dissolution of N and C in the M lattice), which implies a redistribution of the nonmetal atoms among the octahedral interstices of the M sublattice. Kolyagin *et al.*¹⁸⁶ explained the formation of the superstructures by the generation of packing defects of various types in the metallic sublattices of the initial hexagonal close-packed and face-centred cubic phases.

The formation of superstructures in superstoichiometric nitrides with deviations from stoichiometry with respect to the metal is attributed to a redistribution of the M atoms and the structural vacancies in the metallic sublattice.¹⁹ It has been suggested that such structures may be formed as a result of the development of various ordering mechanisms. For example, according to the data of Pushchin and Shagaev,¹⁹⁰ the 3C, 6H₂, 6H, and 4H polytypes were identified by electron microscopy in the Nb–N system on film objects obtained by ionic-plasma sputtering. They are formed in the range of compositions with the ratio M/X close to unity. The 3C polytype is δ-NbN. It is believed¹⁹⁰ that the ordered formation of packing defects in the layers of M atoms of this structure leads to the transition to the 6H and 6H₂ structures, while the combination of such ordering and the ordering of the vacancies entails the appearance of the 4H polytype (Nb₅N₆ — stoichiometric composition).

The formation of multilayer structures is characteristic also of carbides of the type M₇C₃ (M = Cr, Fe). The formation of polytypes based on the monoclinic and rhombohedral modifications of these carbides is associated with the ordered generation of packing defects and microtwinning crystals.¹⁹¹ Indeed, the presence of planar defects such as twinned crystals and antiphase boundaries has been established in the above carbides.¹⁹² These defects may be distributed in the basic lattice of the crystals periodically, quasi-periodically, and randomly and depending on this factor, can give rise to modulated, microdomain, and twinned substructures.

9. Oxygen-containing materials

The polytype formation processes in oxygen-containing materials have been little investigated. We shall therefore consider only the main data available in the literature on this problem.

a. Oxides

BeO. Polytypism in BeO has already been discussed. The known and postulated 2H BeO-based polytypes are presented in Table 7.

2H ZnO. There is no information in the literature about polytypism in 2H ZnO. Our studies established that multilayer polytypes may be formed in the grains of polycrystalline ZnO and ZnO with added ZrO₂. The geometrical and morphological characteristics of crystals under the conditions involving the formation of polytypes are similar to the characteristics of AlN. In particular, the polytypes in the ZnO grains arise in lamellar interlayers segregated along the basal plane, as happens in AlN (Fig. 2).

ZrO_{1/3}. A series of polytypes are formed in the zirconium oxide ZrO_{1/3}, which is obtained on dissolving oxygen in metallic zirconium when the oxygen content varies from 24% to 26%.¹⁹³ They are intermediate structures between the rhombohedral (3R) and hexagonal (2H) modifications, 3R has the composition ZrO_x (*x* < 1/3) and 2H has the composition ZrO_y (*y* > 1.3). The 8H, 5H, 12R, and 7H polytypes arise on the basis of 3R, whereas the 10H, 12H, and 14H polytypes are based on 2H. It has been suggested¹⁹³ that the formation of multilayer structures is determined by the changes in the packing sequence of the oxygen layers. On dissolution in zirconium, oxygen occupies the octahedral interlayer cavities in the face-centred cubic packing. The ZrO_x structure is characterised by an order in the packing of layers of the type ABC ABC..., whilst ZrO_y is characterised by a packing order of the type AB AB.... With increase in the oxygen concentration in zirconium oxide, the sequence in which the number of layers in the polytypes varies is as follows: 3R → 8H → 5H → 12R → 7H → 10H → 9R → 12H → 14H → 2H.

The formation of a set of incommensurate long-period structures in the $\text{ZrO}_2\text{--ZrN}$ system in the region with a high ZrO content (the ZrN content was 2.5 mol.% and more) has been established by electron microscope studies.¹⁹⁴ Similar polytypes have been observed in this system also in another study.¹⁹⁵ It has been suggested¹⁹⁴ that the long-period structures are microstructures produced by the intergrowth of the layers of the basic structure (cubic ZrO_2) and the segregations of the rhombohedral oxynitride $\text{Zr}_7\text{O}_{11}\text{N}_2$, *i.e.* they differ in their phase compositions.

There are data on the formation of multilayer structures in titanium, vanadium, niobium,¹⁹⁶ manganese, and silicon² oxides. In the last case, they are formed on the basis of a polymorphic modification of tridymite. SiO_2 polytypes such as 2H, 4H, 10H, and 20H have been identified.

Multilayer structures have been observed in the orthorhombic aluminium-enriched mullite. The results of studies by high-resolution electron microscopy led to the conclusion¹⁹⁷ that such structures are formed as a result of the ordering of oxygen vacancies. The latter form cavity channels (giving rise to antiphase boundaries) along the *b* axis, the periodic alternation of which actually promotes the formation of multilayer structures. Computer modelling of the structural transitions in mullite with participation of oxygen vacancies confirmed the proposed model of the formation of such structures. It was concluded that the structure formation processes depend on the excess of aluminium.

Polytypism is characteristic also of β -alumina.¹⁹⁸ Two basic forms of alumina, β' and β'' , having the compositions $\text{NaAl}_{11}\text{O}_{17}$ and $\text{Na}_{5/3}\text{Mg}_{2/3}\text{Al}_{21/3}\text{O}_{17}$ respectively, are considered nowadays as the 2H and 3R structures. The formation of two polytypes based on the β'' -form has been observed — 15R and 30R. The polytypes in β'' -alumina differ in the number and regularity of the repetition of oxygen layers of two types. In the first, the oxygen is present at the octahedral and tetrahedral sites, whilst in the second it is present at sites with cubic close packing. The layers of the latter type are conducting. On the basis of the structure of the polytypes, Bovin and Keeffe¹⁹⁸ proposed a new way of designating them: they suggested that the figure corresponding to the number of cationic layers between the conducting layers be enclosed in brackets and added to the usual Ramsdell designation, for example 2H(5), 3R(5), 15R(5), and 30R(5). On decrease in the sodium content in β - Al_2O_3 , the β''' - and β'''' -structures are formed. The number of cationic layers in the structure of the polytypes then increases. The polytypic forms of β''' - Al_2O_3 are designated correspondingly as 2H(7), while those of β'''' - Al_2O_3 are designated as 3R(7).

The polytypism in BaMnO_{3-x} is associated with change in the oxygen concentration. The change in the polytypic composition of this compound on heating has been investigated in the range 1000–1600 °C as a function of the partial pressure of the oxygen in the surrounding medium ranging from 2×10^{-4} to 2×10^{-1} N m⁻¹.¹⁹⁹ In the range of pressures from 2×10^{-1} to 3×10^{-2} N m⁻² with *x* varying from 0 to 0.3, the following polytypes are present in the composition: 15H, 8H, 6H, 10H, and 4H. On increase in *x* from 0 to 0.3 in the temperature range from 1000 to 1600 °C, the following series of polytypes are formed: 2H → 15H → 15H + 8H → 8H + 15R → 8H → 6H → 10H → 4H. For *x* > 0.3, the 4H structure is formed predominantly.

Two polytypic forms are known for SrMnO_3 — α (4H) and β (3C); the perovskite structure is characteristic of the composition SrMnO_{3-x} ²⁰⁰ (in contrast to BaMnO_{3-x} the basic structure of which is 2H).¹⁹⁹

The 4H, 6H, 14H, and 27R polytypes have been identified in barium chromite BaCrO_3 . A model of the structure of the 6H polytype has been proposed.²⁰¹ It is based on the hypothesis of the periodic formation in the basic structure of close-packed BaO_3 layers containing tetravalent chromium atoms in all the octahedral cavities of the oxygen sublattice.

b. Copper-containing metal oxides

Polytypism is characteristic also of layered copper–oxygen compounds belonging to the group of metal oxide superconducting substances. Such compounds are also referred to as cuprates. The available data on polytype formation in substances of this class have been obtained mainly in the study of compounds formed in the following systems: Y–Ba–Cu–O, Bi–Sr(Pb)–Ca–Cu–O, Tl–Ba–Ca–Cu–O, and Hg–Ba–Ca–Cu–O. The polytypes in these substances are regarded as individual phases because they differ in composition. The polytypes are designated by a sequence of figures reflecting the quantitative content of metal atoms in the formula unit, for example $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ is designated by 123, $\text{YBa}_2\text{Cu}_5\text{O}$ by 125, and $\text{BiSr}_2\text{CaCu}_2\text{O}_8$ by 1212.

A common feature of the formation of polytypes in superconducting materials is a tendency towards syntaxy, *i.e.* the formation in individual crystals of a mixture of polytypes (Y–Ba–Cu–O, Bi–Sr–Ca–Cu–O,^{202,203} Hg–Ba–Ca–Cu–O^{204,205}). It has been shown in relation to compounds formed in the Hg–Ba–Ca–Cu–O system that the intergrowth of polytypes in crystals takes place along the same planes, *i.e.* is consistently crystallographically oriented.

The following information is available about the nature of the polytypism in metal oxide superconducting materials. According to Ramesh *et al.*,²⁰⁶ the formation of polytypes is associated with a change in the composition of perovskite blocks. In polytypes of the Y–Ba–Cu–O system, the composition may vary when additional planes, for example Cu–O, are incorporated into the basic structure. These may also be CuO–YO–CuO layers.^{207,208} The results of an electron microscope study of the structure of polytypes have shown²⁰⁹ that such layers are usually segregated in the vicinity of the Cu–O layers existing in the initial structure. The Cu–O layers are displaced relative to one another by 1/2 of the period *b* of the initial tetragonal structure. The number and relative disposition of the Cu–O planes in polytypes vary. This is responsible for the different contents of the quasi-perovskite blocks (*i.e.* the elementary layers bounded by the Cu–O and Cu–O₂ planes) and hence also for the number of layers.²¹⁰ The additional Cu–O layers in the phases of the Y–Ba–Cu–O system have been considered²¹¹ as packing defects. The regular introduction of such layers into the 123 structure (after each Cu–O layer present in the initial phase) promotes the formation of the 248 phase.

According to Alekseevskii *et al.*,^{212,213} the formation of polytypes in superconducting cuprates is determined by the characteristic features of the coupling of the perovskite blocks as elementary constituents of the structure. Two ways of joining such blocks have been proposed. These lead to the formation of polytypes and superstructures.

The principal characteristics of the commonest polytypes in the Y–Ba–Cu–O system have been surveyed²¹⁰ (Table 9). According to the data of Kozo and Wei,²¹⁴ the replacement of Y by Ln in this system leads to a new series of polytypes as individual phases: $\text{LnBa}_2\text{Cu}_3\text{O}_{7-x}$ — Ln123, $\text{Ln}_2\text{BaCuO}_5$ — Ln211, $\text{LnBa}_6\text{Cu}_3\text{O}$ — Ln163, and $\text{LnBa}_4\text{Cu}_3\text{O}$ — Ln143.

The polytypic transitions in the Y–Ba–Cu–O system may also occur on heating,²¹⁵ irradiation by heavy ions,²¹⁶ deformation,²¹⁷ doping by additives such as Co, Fe, and Al,²¹⁸ the replacement of yttrium by the complexes $\text{Cu}_x\text{C}_{1-x}$, and partial replacement of Ba by Ca.²¹⁹

There are numerous publications in which questions concerning the ordering of oxygen atoms and oxygen vacancies in compounds of the Y–Ba–Cu–O system are discussed. According to Chushak *et al.*,²²⁰ the ordering of the oxygen atoms takes place in the basal planes. Ising's model has been used to describe this process.²²¹ On the basis of this model, questions concerning the formation of polytypes in SiC and spinelloids have been discussed.^{13–15} The ordering of the vacancies, accompanied by the formation of superstructures, may be not only one-dimensional but also two- and three-dimensional.²²² The formation of superstructures on the basis of the 123 phase has been reported.²²³

Table 9. Characteristics of the polytypes of the homologous series $Y_2Ba_2Cu_6+nO_{(14+n)\pm x}$.²¹⁰

<i>n</i>	Formula	Phase (poly-type)	No. of CuO planes	<i>K</i> ^a	<i>c</i> / Å	<i>c</i> ₀ / Å ^b	<i>T</i> _c / K ^c
0	YBa ₂ Cu ₃ O _{7-x}	123	1	3	11.763	3.891	91
2	YBa ₂ Cu ₄ O ₈	248 (124)	2	7	27.237	3.891	81.4
1	Y ₂ Ba ₄ Cu ₇ O _{15-x}	247	Alternation of one and two planes	13	50.544	3.888	85.5
4	YBa ₂ Cu ₅ O ₉	125	3	4	15.6	3.90	—
6	YBa ₂ Cu ₆ O ₁₀	126	4	9	34.12	3.791	55

^a The number of elementary layers (quasi-perovskite blocks) in the cell.

^b Thickness of the elementary layer; *c*₀ = *c*/*K*. ^c Temperature of the transition to the superconducting state.

The following polytypes are known for the Bi–Sr–Ca–Cu–O system: 2201, 2212, 2223, 2234, and 2302.^{224–226} It has been suggested that the formation of polytypes in this system is influenced by Pb, which may substitute Bi,²²⁶ and also by the concentrations of Ca and Cu in the crystallisation medium. It has been shown²²⁵ that the 2201 phase, which crystallises in Bi–Sr–Ca–Cu–O glasses, is segregated only in regions depleted in Ca and Cu. The latter occurs as a result of the formation of compounds of the Ca–Cu–O system. The 2223 phase is also segregated under these conditions. The crystals formed in the system considered consist in most cases of a mixture of polytypes, mainly 2223, 2234, and 2212.²⁰³

The crystal-chemical characteristics of the phases formed in the Bi–Sr–Ca–Cu–O system have been examined in detail.²²⁴ It was concluded that the 2201 phase is stoichiometric and can be regarded as the basic structure in this system.

The most characteristic phases in the Tl–Ba–Ca–Cu–O system are 2223 and 2212.²²⁷ In the specific synthesis of the 2223 phase by the application of a high pressure, the 2234 phase is also formed.²²⁸ When Ca is replaced by other metals, new phases are formed, for example on its replacement by magnesium a series of phases may be produced — ranging from 12304 to 12034,²²⁹ while the replacement of thallium by copper results in the appearance of the 2201 phase.²³⁰

The stability of the polytypic structures in Bi- and Tl-containing cuprates were examined as a function of chemical composition²³¹ within the framework of the Ising model with multispin interaction. The compounds in these systems are represented by the homologous series $A_{2x}B_{2x}Ca_{1-x}CuO_{4x+2}$ (*A*, *B* = Bi, Sr or Tl, Ba). It has been shown that, depending on *x*₀, there may be several equilibrium phases (or ideal polytypes):

Phase	2201	2212	2223	4413	0011
<i>x</i> ₀	1	1/2	1/3	2/3	0

For slight deviations of *x* from *x*₀, such phases may be regarded as periodic polytypes containing packing defects. For arbitrary values of *x*, there is a possibility of the combination of a set of disordered phases.

The following main phases have been identified in the Hg–Ba–Ca–Cu–O system: 1212, 1223, 1234, and 1245.²³² They are formed in the synthesis of superconducting phases at both normal²²³ and high²³³ pressures. On combination of the 1212 and 1223 phases and the 1223 and 1234 phases, crystal-oriented intergrowth takes place.²⁰⁴ If Hg and Ca are replaced by Pr, *i.e.* in fact on formation of the new system (Hg, Pr)–(Sr, Ca, Pr)–Cu–O, the 1222 phase is formed together with the 1201 and 1212 phases at the normal pressure.²³⁴

c. Minerals

Polytypism has been observed in a multiplicity of minerals: wollastonite plagioclase, barium feldspar, wenkite, sapphirine;^{18,235} kaolinite, chlorite, pyrosmalite, parasite, synchisite, cronstedtite, hydrotalcite, tridymite, coquimbite;² mica-like minerals, pyrophyllite;^{236,237} ferrite;^{238–240} zirconolite;²⁴¹ spinel;² spinelloids, pyroxenes, and pyroxenoids;^{13,14,242,243} biopyrrol;²⁴⁴ nigerite;²⁴⁵ phyllosilicates;²⁴⁶ silicates containing iron layers — berthierine, glauconites, and biotites.²⁴⁷ (Unfortunately, the available information about the polytypism in minerals is nonsystematic and scattered. Therefore the principal studies in which such information is given are indicated.)

Certain hypotheses concerning the nature of the polytypism in chlorites, micas, and minerals of the kaolinite group, described by Verma and Krishna,² are based mainly on the ideas involving different ways of arranging the layers determining the symmetry and the parameters of the unit cells of multilayer structures. It has been postulated that polytypes are formed *via* the displacement of the layers relative to one another for micas, as a consequence of the periodic introduction of structural packing defects along (100) for wollastonite, and as a result of the appearance of antiphase boundaries along (001) for feldspars.

In micas and mica-like minerals (pyrophyllite, talc), the polytypism is due to the different dispositions in neighbouring layers of pairs of cations which are located along a single normal to these layers.²³⁶ The difference is determined by both the number and kind of the cations superimposed in projection on to the plane of the layer. On the basis of these ideas, the authors deduced the polytypic modifications of micas, and also determined to what extent their formation is favoured by energy factors. A smaller number of superimposed cations constitutes a criterion of their being favoured by such factors.

Polytypes such as 84R, 102R, 40H, and 138R have been identified for hexagonal ferrites.²³⁸ Ideas concerning the nature of the polytypism in such ferrites containing Ca, Ba, Pb, Sr, and K have been described.^{239,240} It has been suggested that the structure of these ferrites is made up of identical spinel type fragments, the so called *S_n* layers, which have two orientations. Layers with both identical and different orientations may be coupled in the structure of the ferrites. Connecting structural elements arise on coupling of the layers. In Ca ferrites, such elements are identical for both types of coupling of the layers, whereas in ferrites containing Ba, Pb, Sr, and K they differ in structure and composition. This factor is actually responsible for the fact that a family of polytypes are formed in Ca ferrites and only fragmentary layered structures are produced in the group of Ba and other ferrites.

The following polytypes are known for the Mg₂Al₄O₈ spinel: 4H, 5H, 6H, 15H, 15R, and 18R.² Horiuchi *et al.*²⁴⁸ established for the first time that a whole family of new structures — spinelloids — are formed on the basis of this spinel structure. In spinelloids, the packing of the oxygen atoms constituting the framework is approximately cubic; they have the ideal stoichiometry corresponding to the composition AB₂O₄. In their structure, 2/3 of the cations occupy sites with octahedral coordination with the oxygen framework; the remaining 1/3 of the cations have tetrahedral coordination. The cations distributed in the oxygen framework constitute the basic structural unit of spinelloids. In the majority of spinelloids, bands are formed on the basis of the packing of the basic structural units, which is invariant in two orthogonal directions. The variation of the arrangement of these bands in three directions actually determines the formation of the set of spinelloid structures. The polytypes in spinels (mainly in the NiAl₂O₄–Ni₂SiO₄ system) have been discussed on the basis of the ANNNI model.^{13,14,242} As already mentioned, a satisfactory agreement between the spin model of polytypism and a real system has in fact been obtained in relation to the family of spinelloid structures.

10. Sulfides

A tendency towards polytype formation has nowadays been discovered in the following sulfides: ZnS, CdS,² FeS, Fe₃S₄,^{12, 18} CuS, NbS₂, TaS₂,^{12, 249} Ti₂S₃,¹² Ti_{1+x}S₂,²⁵⁰ CrNaS₂,¹² ZnIn₂S₄, Zn₂In₂S₅, Zn₂In₂S₄, Zn₃In₂S₆,^{12, 251, 252} GaInS₃,²⁵³ PtS₂, ZrS₂,¹⁵¹ SnS₂, Ti_{1.2}S₂,²⁴⁹ GaS,²⁵⁴ and MoS₂.^{2, 18, 249} This phenomenon has been most thoroughly investigated in the first two sulfides and also in titanium sulfide.^{249, 250, 255} For the remaining sulfides, it has only been established without a detailed discussion and analysis of the characteristics of its occurrence. We shall therefore consider the most interesting data for some of the above series of sulfides.

Hitherto 155 polytypic structures have been identified in ZnS obtained under laboratory conditions; in natural ZnS, only 10 forms have been found: the sphalerite phase and five hexagonal and four rhombohedral polytypes.²⁵⁶

All kinds of polytypism characteristic of substances with the diamond lattice are manifested in ZnS (Table 1).

On heating, the ZnS polytypes are usually formed as intermediate structures in the wurtzite → sphalerite and sphalerite → wurtzite transitions. The first occurs as a rule during the cooling process after synthesis and the second during heating. An intermediate 4H phase is formed in the first transition;²⁵⁷ its appearance in combination with polytypes having a large number of layers is characteristic also of the second transition.

Overall, the polytypic composition of ZnS is influenced by soluble impurities (Cu, Al, O). Their concentration may also stabilise a particular polytype. Thus, according to the data of Kukul',²⁵⁸ the number of layers in the polytypes depends on the Al concentration in the following manner: the 6H polytype is formed mainly for 0.005 mass%, the 4H polytype for 0.04 mass%, and the 2H polytype for 0.1 mass%. With increase in the aluminium and copper content, the concentration of packing defects in ZnS diminishes. It, has been established²⁵⁹ that the decomposition of the solid solution of Cu and O in ZnS promotes the stabilisation of the 3C phase.

The transitions of the hexagonal ZnS polytypes to the 3C phase occur under various load conditions without, special heating: on grinding in a mortar,²⁶⁰ on grinding-polishing,^{261, 262} on oriented (to develop the basal slip) uniaxial loading,²⁶³ and on dynamic compression.²⁶⁴ According to Abdikamalov *et al.*,²⁶³ the conversion of the metastable hexagonal polytypes into the sphalerite phase occurs as a result of plastic displacements in the (0001) plane with the aid of partial Shockley dislocations. It is believed²⁶⁵ that the transition is achieved *via* a layer-by-layer reorientation and may be referred to as deformation recrystallisation.

According to the generally accepted view, the polytypism in ZnS is due to the regular breakdown of the packing of the basal layers as a result of the ordered introduction of packing defects along the (111) and (0001) planes for the 3C and 2H phases respectively. Overall, in the majority of cases the mechanisms of the formation of polytypes in ZnS have been considered not individually but in combination with SiC as a structural analogue. The known theories of the formation of polytypes, briefly considered above in connection with the analysis of the polytypism in SiC, are equally attributed by their authors also to ZnS.

Multilayer polytypes are also characteristic of the compounds Zn₂In₂S₄, Zn₃In₂S₆, and Zn₂In₂S₅, which are formed in the ZnS–In₂S₃ system.^{251, 252} The following structural characteristics have been discovered for such polytypes: the disposition of the indium atoms in the octahedral and tetrahedral cavities and of zinc atoms only in tetrahedral cavities; the presence of layers and packets of cationic vacancies; a marked distortion of the ideal spherical packing of the sulfur atoms. According to the data of Donina *et al.*,²⁵¹ polytypes with the same composition and with identical and different parameters *c* are manifested for the compound Zn₂In₂S₄. A different motif in the alternation of sulfur atoms is characteristic of polytypes of the latter kind.

Polytypes are also formed in the GaInS₃ system.^{253, 266} They have the composition (A,B)_{n-x}S_{n+1} (*n* > 3) and are characterised by the fact that the *n*-stacked layers, consisting of octahedral and

tetrahedral networks, are distributed among close-packed sulfur atoms.

The iron sulfide polytypes have been most thoroughly investigated in relation to pyrrhotites of natural origin (overall formula Fe_{1-x}S) obtained from different deposits.¹⁸ The polytypes of this substance usually differ in the number of iron and sulfur atoms and are considered in most cases as individual stoichiometric phases. For example, the 4C and 2C polytypes have the compositions Fe₉S₁₀ and Fe₁₁S₁₂ respectively. However, there are also polytypes with a wide region of homogeneity, *i.e.* having a non-stoichiometric composition. It has been suggested that the formation of polytypic structures and iron sulfides is associated with the ordering of the metal vacancies in the structure.

The most detailed data about polytypism in the Ti–S system have been published by Palosz²⁴⁹ and Trone and Huber.²⁵⁵ The formation of polytypes with different numbers of layers in the system depends on the temperature.²⁵⁵ The 12R, 12H, 48R, and 696R polytypes are segregated at 800 °C and the 4H, 2H, 8H, 24H, and 40H polytypes are segregated at 900 °C. The polytypes differ in composition: TiS₂ for 2H, Ti_{2+x}S₄ for 4H, and Ti₈S₁₂ for 12R. It has been suggested that the formation of polytypes is associated with the variation of the concentrations of Ti and S atoms in the layers. On this basis, schemes have been proposed for the arrangement of the atoms in the direction of the basal axis for certain polytypes.²⁵⁵

In the compound Ti_{1+x}S₂, ten polytypes with hexagonal and rhombohedral symmetries were identified.²⁵⁰ The presence of screw dislocations in the basal plane has been observed in Ti_{1.18}S₂ crystals by X-ray topography, which may serve as confirmation of the decisive role of these defects in the formation of polytypes.

Data concerning the possibility of the formation of polytypes in MoS₂ and GaS have been published.^{2, 249, 254} The polytypes in MoS₂ may be formed as a result of the alternation of layers with hexagonal and rhombohedral types of packing.²

11. Halides

Among halides tending to form polytypes, one may identify CdI₂, CdBr₂, PbI₂, and AgI; the phenomenon of polytypism has been most thoroughly investigated in these substances.^{2, 249} Polytypes have been observed also in the following halides:¹⁵¹ Mg, Mn, Fe, and Co dibromides and Ti, V, Mn, Fe, Zn, and Co diiodides.

Cadmium and lead dihalides are isostructural. Octahedral coordination of the metal ions is characteristic of these compounds. The 4H, 2H, and 6R (especially 4H) polytypes are most common. Other polytypes have been specified.^{2, 249, 267} The largest number of polytypes (109) have been found for CdI₂.²⁶⁸ It has been suggested that the polytypism in the halides considered is associated with the ordered introduction of structural packing defects.

The following series of polytypes have been identified in AgI: 2H, 4H, 8H, 12H, and 16H.²⁶⁹ The absence of multilayer structures with rhombohedral symmetry as well as the widest occurrence of the 4H polytype should be included among the characteristic features of the formation of polytypes in this substance.²

12. Selenides and tellurides

Polytypism is characteristic of the following substances in the group of selenides: InSe,^{12, 254} GaSe,^{254, 270} CdSe,²⁷¹ ZnSe,²⁷² SnSe,²⁴⁹ TaSe₂, NbSe₂, Bi₂Se₃, In₂Se₃, and Pb₂Bi₂Se₅.¹² Few data are available on the formation of polytypes in these substances. The 24H polytype has been identified by X-ray diffraction in the CdSe crystals obtained from the gas phase.²⁷¹ According to the data of Ollitrault-fichet *et al.*,²⁷⁰ the following series of polytypes have been observed in GaSe: 4H, 9R, 12R, and 15R. The 2H, 4H, and 3R polytypes are known for TaSe while the 2H,²¹⁰ and 4H (see Ref. 2) polytypes are known for NbSe₂.

Polytypes are also known in the group of tellurides: CdTe, ZnTe,²⁷³ In₃Te₄, Se₂Te₃, and Ge₂Te₃.¹² The 15R and 2H poly-

types have been identified in ZnTe crystals grown from the gas phase; the 12H polytype, contained in the 3C phase, has been found in CdTe crystals obtained under analogous conditions.

Among the gallium compounds, polytypism has been observed in GaSe,²⁵⁴ GaP,²⁷⁴ and GaAs.²⁷⁵ The 6H polytype has been identified in the last compound.

III. Practical aspects of polytypism

The influence of polytypism on the properties of nonmetallic crystalline materials has been little studied. We shall consider this problem in relation to several materials.

Various SiC polytypes (mainly 3C, 6H, 4H, 15R, 8H, and 10H) are distinguished by the following properties: the width of the forbidden band; the width of the exciton forbidden band; the effective mass of free electrons; the Hall mobility of electrons; electrical conductivity; luminescence; the energy of phonons; ionisation energy; relative permittivity; the minimum in the conductivity band both as regards position and energy.^{2, 6, 38, 39, 276–279} Other properties of the polytypes also differ.^{280, 281}

The differences in the electrophysical properties of the SiC polytypes make it possible to regard them as a family of wide-band semiconducting materials; However, owing to the difficulty of growing crystals and films with a specified polytypic composition, only the 6H polytype of silicon carbide is used nowadays as a semiconducting material.²⁷⁹

By regulating the polytypic transitions in SiC (3C → 6H, 3C → 4H, 6H → 4H), it is possible to control the subgranular and granular structures in polycrystalline materials. Such transitions promote the formation of a one-dimensional microplastic substructure in the grains, the development of anomalous recrystallisation leading to the formation of self-reinforced materials, and the occurrence of collective recrystallisation of the 'grain to grain type'. Questions concerning the formation of self-reinforced SiC materials of different types have been examined.^{87, 282} It has been shown that the addition of boron, aluminium, and their compounds, which activate the 3C → 4H and 6H → 4H transitions, is effective for the preparation of such materials. The self-reinforced SiC materials are very strong and are distinguished by chemical and structural stability at elevated temperature (> 1300 °C). The latter is determined by the presence of reinforcing grains in the form of plates bounded by basal surfaces; the shape factor for such grains may amount to 10–20. It follows from the data quoted by the present author⁸⁷ that the bending strength of the self-reinforced materials may reach 1000 MPa and may change insignificantly with increase in temperature up to 1500 °C.

The formation of polytypes in aluminium nitride has the opposite effect on properties such as thermal conductivity and strength. With increase in the number of multilayer polytypes in the AlN + Al₂O₃ and AlN + SiO₂ the polycrystalline materials, the thermal conductivity diminishes.^{283, 284} This is induced mainly by the increase in the length of the interfaces between different structural states in the material as a result of the segregation of polytype interlayers within the grains or of grains consisting of multilayer polytypes. The formation of polytypes in AlN, like that in SiC, promotes the formation of self-reinforced materials. The mechanism of the formation of such materials has been examined in detail.⁸⁵ It is possible to obtain three types of microstructure of the self-reinforced AlN. Such microstructures may be made up, firstly, of grains reinforced by interlayers, comprising polytypes in the form of plates. Secondly, they can be produced by the combination of grains with interlayers and fragments of individual grains in a lamellar form; thirdly, they can consist predominantly of lamellar grains. The microstructure of the second type is the most characteristic (Fig. 15). Our studies established that three types of grains and six varieties of interfaces can be distinguished in a material with such microstructure.²⁸⁵ The nature of the differences between the grains is fully determined

by the presence of the AlN polytypes in the material. All the varieties of grains and interfaces are noted in the scheme in Fig. 15 and their most typical combinations and morphological characteristics are also shown.

The formation of self-reinforced AlN materials, due to deformation of polytypes as in the case of SiC, is a positive factor. Such materials are distinguished by improved strength properties at both normal and elevated temperatures. Data indicating the strengthening of the AlN materials obtained under the conditions of polytype formation with oxygen-containing additives such as TiO₂, MoSi₂, TiC, and TiN (in the last three compounds, the

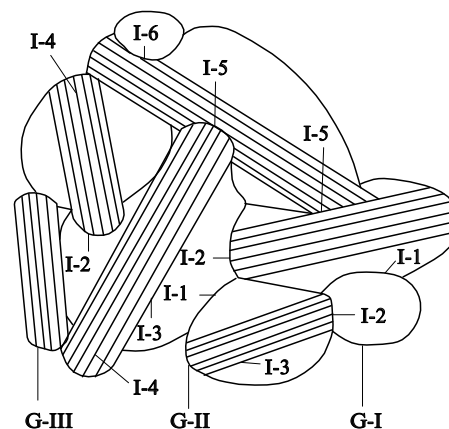


Figure 15. Schematic illustration of the microstructure of a self-reinforced AlN material characterised by the presence of three types of grains and six varieties of internal interfaces. Grain composition: G-I — 2H AlN–O solid solution; G-II — 2H–AlN matrix combined with a plate made up of MP; G-III — individual MP grains; I-1, I-2, I-5, I-6 — intergranular interfaces; I-3, I-4 — intragranular interfaces.

oxygen is present as an impurity) have been published.²⁸⁶ The results presented by the present author⁸⁷ indicate that self-reinforced AlN materials retain their strength up to 1500–1600 °C. Consequently such materials may be used also at high temperatures.

On the basis of the ideas concerning the formation of polytypes in AlN developed by Oleinik and Shevchenko¹⁴² and the analysis of a large number of literature data on this process in AlN materials, it is possible to formulate the physicochemical principles governing the selection of additives to AlN in order to obtain constructional and heat conducting materials. These principles take into account two evident factors. Firstly, in virtually all AlN powders obtained by different methods there is bound oxygen on the surface (aluminium oxides, hydroxides, or oxynitride).²⁸⁷ Secondly, the formation of polytypes as a necessary stage in the structural preparation for the production of a self-reinforced material occurs under conditions involving the formation of the 2H AlNO solid solution, which is stable up to 1700 °C and is formed with the appearance of vacancies in the aluminium sublattice.

Since the vacancies promote a decrease in the thermal conductivity of AlN,²⁸⁸ it is necessary to refine AlN with respect to oxygen or to neutralise the vacancies in order to obtain materials for heat-conducting purposes. The preparation of materials involving the formation of AlN polytypes requires the use as additives of either oxides which do not form stable compounds with Al₂O₃ up to 1700 °C and the dissolution of the cations of which in AlN does not promote charge compensation in the lattice on substitution of nitrogen by oxygen or nonoxide compounds (these are a source of oxygen as an accompanying impurity) which do not form stable compounds with oxygen up to 1700 °C and the dissolution of which in AlN does not promote charge compensation in the lattice on substitution of nitrogen by oxygen.

The following approaches have to be used in order to create materials for heat-conducting purposes.

Firstly, it is necessary to use as additives oxides which form stable compounds with Al_2O_3 up to 1700°C and their stability is higher than that of the 2H AlNO solid solution at $T > 1700^\circ\text{C}$ (Y_2O_3 and CaO are the most effective) and oxides which do not interact with Al_2O_3 and the joint dissolution of the cations and anions of which ensures the charge compensation of the AlN lattice (a typical example of such an additive is BeO).

Secondly, it is necessary to sinter the materials at high pressures and temperatures. Since the formation of vacancies is difficult at high pressures, the 2H AlNO solid solution is not formed. The oxygen contained in the initial AlN powder is bound as Al_2O_3 , which is segregated as disperse particles along the grain boundaries in the sintered material.¹³² Data concerning the formation of a AlN material with a thermal conductivity up to $185\text{ W m}^{-1}\text{ K}^{-1}$ ²⁸⁹ constitute convincing confirmation of this. Our investigations established²⁹⁰ that preliminary treatment of the initial powder in shock waves promotes the refining of AlN on subsequent sintering *via* the formation of oxygen-containing disperse segregations in the grain boundaries.

The polytypes of copper-containing metal oxide compounds (cuprates) are distinguished by the temperature of the transition to the superconducting state (T_c). This is caused by their different contents of conducting copper-containing layers. As an example, one may point to data on T_c obtained²⁹¹ for certain polytypes of the $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$ homologous series (n is the number of CuO_2 layers). The 2201 ($n = 1$), 2212 ($n = 2$), and 2223 ($n = 3$) phases have $T_c = 7, 80$, and 110 K respectively. It has been shown by means of model calculations that T in phases with $n > 4$ may reach 142 K .

The relation between c_0 and T_c has been discovered (Table 9).²¹⁰

Another group of substances which tend to form polytypes and in which this phenomenon has a useful application are the carbides and nitrides of the type of interstitial phases. The conversion of the structure of these phases into a microdomain form, associated with the formation of multilayer structures, is known to strengthen the phases. The degree of strengthening is then determined by the size (the thickness of the cross-section) of the domains, which may be regulated by altering the rate of cooling.²⁹²

IV. Conclusion

The data described permit several general and specific (referring to particular groups of substances) conclusions about the formation of polytypes in nonmetallic materials.

Polytypes are formed both at normal and high temperatures and pressures. Their formation reaction occurs in substances in the form of powders, films (single-crystal and polycrystalline), isolated single crystals, and compact polycrystalline materials; the reaction is characteristic of substances with different energies of the packing defect (from $5.4 \pm 1.8\text{ mJ m}^{-2}$ for ZnS to $279 \pm 41\text{ mJ m}^{-2}$ for diamond),²⁹³ different types of crystal lattice, and different types of chemical bonds; it can occur both during the growth of the crystals and films and on treatments of different kinds (heating, doping, deformation, irradiation, *etc.*).

Polytypic transitions may be of two kinds depending on the nature of their development: intracrystallite and intercrystallite. The intragranular formation of polytypes is associated with the periodic formation of planar defects of different types in the basic structure.

For example, such defects in SiC, ZnS, CdS, CdI_2 , CdBr_2 , PbI_2 , Si, C (graphite, 2H), BN (graphite-like), and wollastonite are structural packing defects; for B_4C , BN (3C), C (3C), and M_7C_3 ($\text{M} = \text{Fe, Cr}$), these are microtwinning crystals; for mullite and barium feldspar, these are antiphase boundaries; for FeS and $\text{Zn}_3\text{In}_2\text{S}_6$, they are layers of ordered vacancies; for Group IV–VI transition metal carbides and MoS_2 , they are layers with face-

centred cubic or hexagonal close packing; for BeO, BeSiN_2 , ZrO_2 , AlN, and $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, they are layers of other phases. Defects consisting of layers differing from the basic structure by the elemental composition and packing of atoms ($\beta\text{-Al}_2\text{O}_3$), the disposition of cations in adjoining layers (micas, talc), the motif in the alternation of like layers ($\text{Zn}_2\text{In}_2\text{S}_4$), the number of constituent like atoms (compounds in the Ti–S system), the coordination number of like atoms (BaCrO_3), and the arrangement of basic structural units (spinelloids, zirconolite) are characteristic of certain ceramics; planar defects in the arrangement of chains of SiO_2 tetrahedra are typical for hexagonal ferrites and biopyrrol.

The presence of defects such as the elements of the structures of polytypes in many substances (for example, SiC, AlN, BeSiN_2 , and BN) has been confirmed experimentally and in many instances their formation has been postulated on the basis of crystal-chemical and substructural characteristics of substances. Intergranular polytypic transitions have now been discovered only for substances with diamond-like lattices (SiC, AlN, BN). They are due to diffusion and occur in the following cases: (a) on migration of the boundary between grains made up of different polytypes (SiC, AlN — Fig. 3); the development of such transitions is always preceded by intragranular crystal-oriented phase and (or) polytypic transformations;⁸⁶ (b) under the conditions of recrystallisation *via* a liquid phase (deposition of 6H SiC layers on a 6H SiC support on recrystallisation of the 3C phase *via* eutectic melts of metals);²⁹⁴ (c) on recrystallisation *via* the gas phase (sublimation growth of crystals and films).²⁷⁹

In many substances, the polytypes differ in composition, *i.e.* they actually constitute a set of stoichiometric phases. The most typical representatives of such substances are AlN, BeO, BeSiN_2 , ZrO_2 , superconducting ceramics, and compounds in the Ti–S, Fe–S, *etc.* systems.

In the group of diamond-like phases, the energy of the packing defects exerts an appreciable influence on the type of planar defects in the basic lattice, *i.e.* on the block coupling boundaries consisting of layers with identical packing of the atoms.

In the case of low energy of the structural packing defects, the formation of polytypes is determined by this type of planar defects regardless of the formation conditions. SiC and ZnS, in which all kinds of polytypism occur (growth, deformation, and concentration polytypism), may serve as a typical example.

In substances with a diamond-like structure, a high fraction of ionic bonding, and a high packing defect energy (AlN, BeO, BeSiN_2), a special type of concentration polytypism occurs as a result of the regular segregation of two-dimensional layers of the second phase in the basic layers of the 2H structure. Different polytypes in substances of this group may be represented by a consecutive series of ordered stoichiometric phases corresponding to a definite ratio M/X.

The formation of multilayer polytypes based on cubic phases on carbon and BN at high temperatures and pressures indicates the possibility of the transition of these phases to dense hexagonal ones, *i.e.* lonsdaleite and 2H BN respectively. This can be accounted for as follows: In polytype formation processes in diamond and 3C BN in the region of their thermodynamic stability, a decisive influence on the development of this process is exerted not by the chemical driving force (it is the driving force of the phase transition) but by the stresses arising under the influence of an external load. The latter is due to the fact that the geometry of the plastic displacements, inevitably arising on deformation in the cubic phases of diamond and BN, coincides with the slip geometry inducing the deformation rearrangements of these phases to dense hexagonal phases.

The formation of polytypes during growth and the polytypic transitions on treatment (heating, doping, deformation) in the bulk of nonmetallic crystals are processes involving a relaxation structural rearrangement, which takes place *via* the regular formation of planar defects of different nature in the crystal lattice. Such defects are produced mainly in only one crystallo-

graphic direction. This is responsible for the regular modulation of the lattice parameter of the basic structure and for the formation of a new structure from it and modulating defects. The nature of the planar defects is determined by the crystal geometry of the lattice of the substance, which determines the energetically favourable structural relaxation mechanism. The minimum lattice energy increment following the introduction of defects is determined by three factors: the nature of the defects, the mechanism of their coupling with the basic (matrix) structure, and the nature of the distribution of defects determining the minimisation energy of their interaction (elastic, electronic, phonon, etc.).

Intercrystallite polytypic transitions may occur for diamond-like phases (SiC, AlN, BN). Their development is determined by the orienting effect of the force field of the crystal-support lattice. In this case, we have only the inheritance of the packing order of the atoms of the polytype-support in the layer formed on the support as a result of the recrystallisation of another polytype *via* the solid, liquid, and gas phases.

It appears that at the present time there are grounds for classifying polytypism as the fourth kind of fundamental structural rearrangement (together with the three classical kinds — plastic deformation, polymorphic transformation, and recrystallisation). Like the known types of rearrangements indicated above, polytypes may be formed not *via* one but *via* several structural mechanisms of the transformations.

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Ion exchange on inorganic sorbents

A B Yaroslavtsev

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Abstract. The principal features of the thermodynamics and kinetics of ion-exchange processes in inorganic ion exchangers are discussed. The literature data on the ion-exchange properties of oxide systems, globular hydrates, and salts of polyvalent cations are surveyed. The methods for carrying out ion-exchange processes and the characteristic features of their occurrence on typical inorganic ion-exchange materials are examined. The bibliography includes 306 references.

I. Introduction

Ion exchange on inorganic substances is characteristic of many natural and industrial processes. Even before the demonstration of the existence of ions as such, it was observed that treatment of soil specimens with solutions of ammonium salts entailed the reversible formation of calcium salts.^{1,2} It was established that this is due to the presence of a series of clay minerals in soil. The first synthetic ion-exchange materials were later obtained — amorphous sodium aluminosilicates, which were used successfully to reduce the hardness of water.³ Amorphous and crystalline substances of this type, called zeolites, were for a long time the main objects for the study of ion-exchange processes. A significant disadvantage of zeolites proved to be their low stability in experiments in highly acid and alkaline solutions. This stimulated chemists to seek new materials with analogous properties. Synthetic ion exchangers on a polymer matrix — ion-exchange resins⁴ — rapidly displaced the inorganic analogues.

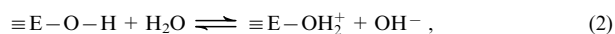
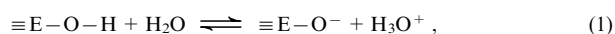
The revival of interest in inorganic sorbents began in the early 1960s. This was associated with the fact that ion exchangers with a fairly high thermal stability and resistance to ionising radiation were needed for many branches of industry; furthermore, an extremely high partition coefficient was observed in certain inorganic sorbents even for alkaline earth metal cations, which are comparatively difficult to separate. After the synthesis by Clearfield and Stynes⁵ of the cryptocrystalline acid zirconium phosphate, which is now one of the most familiar inorganic ion exchangers, the stream of studies devoted to ion exchange on inorganic materials increased significantly. Crystalline zirconium

phosphate is distinguished by a higher stability, compared with amorphous specimens, and a higher sorption capacity compared with zeolites. By employing it, it is possible to observe the structural changes in the substance in the course of the exchange. The latter stimulated a series of purely theoretical investigations.

However, one should note that there have been comparatively few review publications on the study of inorganic ion exchangers. Among these, one may point to Amphlett's monograph,⁶ a book edited by Clearfield,⁷ as well as the review by the latter,⁸ devoted mainly to the description of the properties of various classes of ion-exchange substances. The remaining publications are more specific. The aim of the present review is a survey of the thermodynamic and kinetic ideas about ion exchange on inorganic matrices and also the use of these data for the analysis of the properties of various compounds, results that have not so far entered into review publications being emphasised.

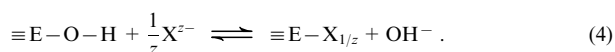
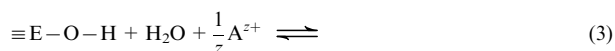
II. Thermodynamics of ion exchange

When substances containing groups of $\equiv\text{E}-\text{O}-\text{H}$ fragments accessible to the exchange of H^+ and OH^- come into contact with an aqueous solution, an equilibrium that is determined by the occurrence of the following reactions is established in the system:



where E is a polyvalent element.

As a result, the entire volume of the substance or a proportion of it acquires a negative or positive charge and sorption from a solution of cations or anions becomes possible:



The tendency of a substance to manifest cation- or anion-exchange properties is determined primarily by the acidity of the $\equiv\text{E}-\text{O}-\text{H}$ groups. Zirconium hydrogenphosphate $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ is known to contain O_3POH groups the proton-accepting capacity of which is reduced as a result of their coordination to a cation with an appreciable polarising capacity. These groups tend to dissociate only *via* reaction (1) and the compound exhibits only cation-exchange properties.^{8,9} The hydroxyapatites $[\text{Ca}_x(\text{PO}_4)_y(\text{OH})_{2x-3y}]$ and the hydrogelcites having the compositions

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$[M_3^{II}M^{III}(OH)_8]^+x_{1/z}^-$, or $[M_2^{II}M^{III}(OH)_6]^+x_{1/z}^-$,¹⁰ as well as certain complex oxides¹¹ dissociate in accordance with reaction (2) and these substances therefore exhibit anion-exchange properties. Finally, both types of dissociation are characteristic of a series of compounds. This applies in the first place to the large class of hydrated oxides of Group III and IV elements such as aluminium, gallium, tin, and zirconium. The degree of conversion for reactions (1)–(4) and the ion-exchange capacities themselves of these compounds depend significantly on the method of synthesis of the latter and the acidity of the medium. Analysis of the dependence of the ion-exchange capacities of hydrated oxides on the pH of the medium, presented in Fig. 1, shows that the position of the equivalence point for the series of zirconium, tin, and silicon oxides diminishes from ~7 to ~6 and ~2 in strict correspondence with the decrease in the basicities of these compounds; the exchange of anions is altogether not characteristic of $HSbO_3 \cdot H_2O$. Since inorganic sorbents are distinguished by a high selectivity, the position of the equivalence point depends also on the nature of the sorbed ions.

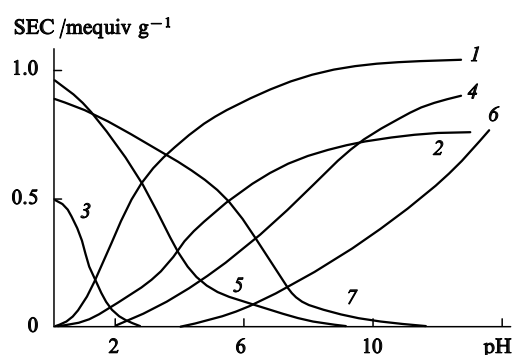


Figure 1. Dependence of the sorption exchange capacities (SEC) of the hydrated oxides of antimony (1), silicon (2, 3), tin (4, 3), and zirconium (6, 7) on the pH of the medium in the sorption of sodium (1, 2, 4, 6) and chloride (3, 5, 7) ions. The figure has been constructed on the basis of data from Kraus *et al.*¹² and Ahrlund *et al.*¹³

It is noteworthy that, among the inorganic materials used as ion exchangers, cation exchangers are more common than anion exchangers. Anions have larger radii and this creates steric hindrance to their insertion into the bulk of the specimen. Furthermore, for the manifestation of anion-exchange activity by a substance, the latter must contain hydroxy-groups and must be able to substitute them by anions. However, the salts of polyvalent elements the OH groups of which more often possess distinctly acid properties show a greater tendency to sorb cations. In view of this, the thermodynamic features of ion exchange will henceforth be considered in relation to cations.

For reaction (3), which proceeds *via* a stage involving the formation of the solid solutions $xR-O-A_{1/z} \cdot yR-O-H$, the thermodynamic equilibrium constant may be represented by the expression

$$K_a = \frac{a(H_3O^+)_{\text{soln}} a(A^{z+})_s}{a(H_3O^+)_s^z a(A^{z+})_{\text{soln}}}, \quad (5)$$

where a are the activities of the corresponding cations in solution (soln) and in the solid phase (s). By expressing the activity as the product of the concentration (c) and the activity coefficient (γ), we obtain

$$K_a = \frac{c(H_3O^+)_{\text{soln}}^z \gamma(H_3O^+)_{\text{soln}}^z c(A^{z+})_s \gamma(A^{z+})_s}{c(H_3O^+)_s^z \gamma(H_3O^+)_s^z c(A^{z+})_{\text{soln}} \gamma(A^{z+})_{\text{soln}}}, \quad (6)$$

or, for the concentration equilibrium constant, we have

$$K_c = \frac{[H_3O^+]_{\text{soln}}^z [A^{z+}]_s}{[H_3O^+]_s^z [A^{z+}]_{\text{soln}}} = \frac{K_a \gamma(H_3O^+)_{\text{soln}}^z \gamma(A^{z+})_{\text{soln}}}{\gamma(H_3O^+)_s^z \gamma(A^{z+})_s}. \quad (7)$$

A certain complication arises because the activity coefficients of the cations in the solid phase are difficult to estimate. On the other hand, in order to determine the thermodynamic functions of the exchange reactions it is necessary to know the thermodynamic equilibrium constant. Gaines and Thomas¹⁴ proposed the following procedure for this purpose. The so-called 'mixed' equilibrium constant

$$K_{ac} = \frac{a(H_3O^+)_{\text{soln}}^z N(A^+)_{\text{s}}}{N(H_3O^+)_s^z a(A^+)_{\text{soln}}}, \quad (8)$$

where N is the mole fraction of the corresponding cation in the solid phase, is calculated initially. The thermodynamic constant is found from the relation

$$\ln K_a = \int_0^1 \ln K_{ac} dN(A^+)_{\text{s}} \quad (9)$$

It is noteworthy that the equilibrium exchange constant is usually not a constant quantity as a consequence of the change in the entropy of the system on contamination of the cationic sublattice of the initial substance or the product by microamounts of an impurity in the initial and concluding stages of the exchange reaction.^{15–18}

Furthermore, in layered compounds the interplanar spacing and the size of the coordination polyhedra itself vary in the course of the exchange from values typical for the ion to be substituted to those characteristic of the incoming ion. The enthalpy and Gibbs free energy of exchange therefore decrease, while the equilibrium constant increases somewhat as the process proceeds (Fig. 2).

In many inorganic ion-exchange substances, the exchange proceeds in a two-phase region — the region corresponding to the existence of the substituted and unsubstituted forms. The process then takes place as a result of the displacement of the interface between these phases for a virtually unchanged composition of the latter. The formation of two phases during exchange on layered acid phosphates of tetravalent elements [α -Ti(HPO₄)₂ and α -M^ITiH(PO₄)₂ or α -M^ITiH(PO₄)₂ and α -M^ITi(PO₄)₂] may

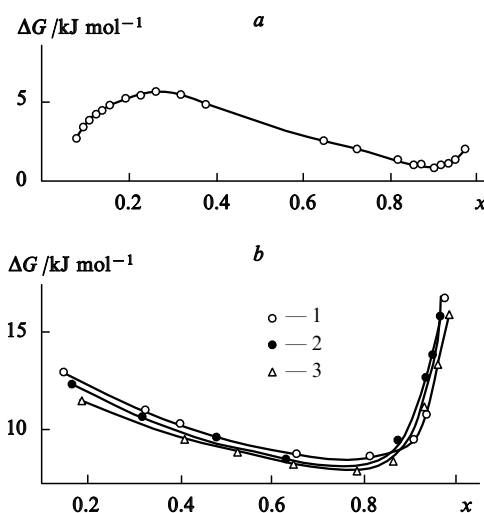


Figure 2. Dependence of the Gibbs free energy on the degree of substitution of the proton (x) in $K_xH_{1-x}Ta(PO_4)_2$. The figure has been constructed on the basis of data from Guarido *et al.*,¹⁵ Rullberg and Clearfield,¹⁶ Yaroslavl'tsev *et al.*,¹⁷ and Yaroslavl'tsev and Khrulev.¹⁸ (a) Overall curve; (b) for titration of the alkaline product of the interaction of $H_2O_2Ta(PO_4)_2$ with an excess of the corresponding alkali metal chloride: (1) NaOH; (2) LiOH; (3) KOH.

Table 1. Thermodynamic parameters of certain ion-exchange processes on inorganic sorbents.

Initial phase	Substituted phase	K_{298}	ΔG_{298} /kJ mol ⁻¹	ΔH_{298} /kJ mol ⁻¹	ΔS /J mol ⁻¹ K ⁻¹	Ref.
Attapulgit (Li ⁺)	Attapulgit (Cs ⁺)	0.029	8.9	17	25	21
Attapulgit (Na ⁺)	Attapulgit (Cs ⁺)	0.041	8.0	16	24	21
Attapulgit (K ⁺)	Attapulgit (Cs ⁺)	0.13	5.1	12	24	21
Montmorillonite (K ⁺)	Montmorillonite (Cs ⁺)	0.076	6.3	—	—	22
		(293 K)	(293 K)			
Montmorillonite (Sr ²⁺)	Montmorillonite (Cs ⁺)	1.9×10^{-3}	15.5	27	25	22
Montmorillonite (Y ³⁺)	Montmorillonite (Cs ⁺)	3.8×10^{-4}	19.7	28	27	23
		(303 K)	(293 K)			
Vermiculite (Li ⁺)	Vermiculite (Na ⁺)	7.7	-5.0	-21.3	-55	6
Shabasite (Na ⁺)	Shabasite (Ag ⁺)	11.4	-6.0	—	—	24
Clinoptilolite (Na ⁺)	Clinoptilolite (Th ⁴⁺)	0.26	3.33	—	—	25
Mordenite (Na ⁺)	Mordenite (Th ⁴⁺)	0.20	3.94	—	—	25
(NH ₄) ₃ PMo ₁₂ O ₄₀	K ₃ PMo ₁₂ O ₄₀	4	-3.4	—	—	26
	Rb ₃ PMo ₁₂ O ₄₀	192	-13.0	—	—	26
	Cs ₃ PMo ₁₂ O ₄₀	5500	-21.3	—	—	26
Zr(HPO ₄) ₂ ^a	Li ⁺ - Zr(HPO ₄) ₂	0.03	8.4	0	-28	27
	Na ⁺ - Zr(HPO ₄) ₂	0.16	4.6	-11	-54	27
	Na ⁺ - Zr(HPO ₄) ₂	0.02	9.7	-14	-77	28
	K ⁺ - Zr(HPO ₄) ₂	0.4	2.3	-24	-88	27
	Rb ⁺ - Zr(HPO ₄) ₂	48	-9.6	-40	-104	29
	Rb ⁺ - Zr(HPO ₄) ₂	1.8	-1.4	-32	-103	30
	Cs ⁺ - Zr(HPO ₄) ₂	2.7	-2.5	-36	-105	28
	Cs ⁺ - Zr(HPO ₄) ₂	81	-10.9	-42	-105	29
	Cs ⁺ - Zr(HPO ₄) ₂	4.8	-3.9	-37	-110	30
	Ca ⁺ - Zr(HPO ₄) ₂	0.04	8.1	-3.6	-39	29
	Sr ²⁺ - Zr(HPO ₄) ₂	0.06	7.1	4.4	-4	29
	Ce ³⁺ - Zr(HPO ₄) ₂	0.10	5.6	2.7	-7	29
Zr(O ₃ PC ₆ H ₄ SO ₃ H) _{0.43} (HPO ₄) _{1.57}	Na ⁺ - ZPP	0.90	0.27	-8.3	-29	31
	Cs ⁺ - ZPP	50	-9.7	-15.9	-21	31
	Mg ²⁺ - ZPP	3.6	-3.2	0.9	14	31
	Na ⁺ - ZPP	91	-11.2	-2.7	28	31
α-Ti(HPO ₄) ₂	α-TiHLi(PO ₄) ₂	5.2×10^{-4}	18.7	0.0	-63	32
	α-TiHLi(PO ₄) ₂	3.0×10^{-4}	19.6	—	—	18
α-TiHLi(PO ₄) ₂	α-TiLi ₂ (PO ₄) ₂	2.1×10^{-4}	21.0	-0.2	-71	32
	α-TiLi ₂ (PO ₄) ₂	5×10^{-6}	28.9	—	—	18
α-Ti(HPO ₄) ₂	α-TiHNa(PO ₄) ₂	1×10^{-3}	16.6	—	—	18
α-TiHNa(PO ₄) ₂	α-TiNa ₂ (PO ₄) ₂	3.7×10^{-6}	31.1	—	—	18
α-Ti(HPO ₄) ₂	α-Ti(KPO ₄) ₂	3×10^{-6}	31.2	15.5	-52	15
	α-Ti(KPO ₄) ₂	8.9×10^{-7}	34.5	—	—	18
γ-Ti(HPO ₄) ₂	γ-TiH _{1.5} Li _{0.5} (PO ₄) ₂	0.35	2.6	3.7	3.8	33
	γ-TiH _{1.5} Li _{0.5} (PO ₄) ₂	0.11	5.4	7.8	8	34
	γ-TiH _{1.5} Na _{0.5} (PO ₄) ₂	0.80	0.55	1.2	2.3	33
	γ-TiH _{1.5} K _{0.5} (PO ₄) ₂	1.8	-1.5	-1.1	1.6	33
	γ-TiH _{1.5} Cs _{0.5} (PO ₄) ₂	3.9	-3.4	-2.4	3.4	33
	γ-TiH _{1.5} Cs _{0.5} (PO ₄) ₂	17.6	-7.1	-5.1	7.0	35
γ-TiH _{1.5} Li _{0.5} (PO ₄) ₂	γ-Ti(LiPO ₄) ₂	0.3	3.0	-4.2	-24	33
	γ-Ti(LiPO ₄) ₂	0.08	6.3	-8.8	-51	34
γ-TiH _{1.5} Na _{0.5} (PO ₄) ₂	γ-Ti(NaPO ₄) ₂	0.5	1.6	-3.3	-17	33
γ-TiH _{1.5} K _{0.5} (PO ₄) ₂	γ-Ti(KPO ₄) ₂	0.9	0.17	-2.9	-10	33
γ-Ti(HPO ₄) ₂	γ-TiH _{0.5} Cu _{0.5} (PO ₄) ₂	0.16	4.6	35.5	104	36
Sn(HPO ₄) ₂ ^a	Na ⁺ - Sn(HPO ₄) ₂	0.3	3.1	-1	-29	37
	K ⁺ - Sn(HPO ₄) ₂	9	-5.3	-15	-33	37
	Rb ⁺ - Sn(HPO ₄) ₂	50	-9.5	-22	-42	37
	Cs ⁺ - Sn(HPO ₄) ₂	125	-11.7	-17	-24	37
Ce(HPO ₄) ₂ ^a	Li ⁺ - Ce(HPO ₄) ₂	2.8	-2.5	0.9	11	38
	Na ⁺ - Ce(HPO ₄) ₂	1.0	0.0	0.8	3	38
	K ⁺ - Ce(HPO ₄) ₂	2.7	-2.5	-0.2	3	38
TaH(PO ₄) ₂	TaLi(PO ₄) ₂	0.2	4	-35	-130	39
	TaNa(PO ₄) ₂	0.6	1	-36	-140	39
	TaK(PO ₄) ₂	0.3	3	8	12	39

Note. All the thermodynamic parameters were calculated for substitution of one mole of cations. ^a Amorphous.

serve as a typical example. The procedure for the determination of the thermodynamic parameters of the exchange described above is therefore inapplicable for compounds of this kind, but it has been used nevertheless in a large number of studies. Since the activities of the incoming cations A^{z+} and of the hydrogen in the solid phase remain constant, the equilibrium constant should be expressed by the relation¹⁸

$$K_a = \frac{a(H_3O^+)_{\text{soln}}}{a(A^{z+})_{\text{soln}}} = \frac{[H_3O^+]_{\text{soln}} \gamma(H_3O^+)_{\text{soln}}}{[A^{z+}]_{\text{soln}} \gamma(A^{z+})_{\text{soln}}} = \frac{K_c \gamma(H_3O^+)_{\text{soln}}}{\gamma(A^{z+})_{\text{soln}}} \quad (10)$$

The error due to the calculation of the equilibrium constant using Eqns (6) and (7), which are erroneous for the given process, is to a large extent abolished on further mathematical treatment with the aid of Eqn (9). For this reason, the values of K_a and of the free energy of exchange obtained with the aid of this procedure may approach the true values.

There are several standard approaches to the description of the ion-exchange equilibrium. A number of workers have investigated the equilibrium after adding a definite amount of a salt to the ion exchanger in the hydrogen-form (hydroxo-form) and the reaction is frequently carried out with microamounts of a salt, which makes it possible to describe the equilibrium only in the initial stages of the exchange process. The most promising method involves the study of the curves for the titration of cation exchangers with alkali in the presence of a salt of the corresponding metal. The process then reduces to the neutralisation of the acid produced. This makes it possible to carry out experiments only in acid and weakly alkaline media and to reduce to a minimum the effect of hydrolysis even for readily hydrolysable compounds such as, for example, tantalum hydrogenphosphate.¹⁷ In order that the exchange of ions occurs *via* the stage involving the formation of solid solutions, the concentration of hydrogen ions $[H^+]$ should vary in proportion to the mole fraction of the protons in the solid phase [in accordance with Eqn (8)]. For layered hydrogenphosphates of polyvalent elements, the equilibrium involving solid phases with different degrees of substitution should seemingly lead to a constant overall concentration of protons and metal cations.⁶ However, when alkali is added, the concentration diminishes somewhat owing to the neutralisation reaction. For this reason, the titration curve is skewed for all the processes described in the literature.^{19, 20}

Certain values of the thermodynamic parameters for exchange reactions on inorganic sorbents are presented in Table 1. It is noteworthy that the significant discrepancies between the parameters for the sorption of alkali metal cations on amorphous zirconium phosphate are due to the difference between the methods used to determine the required quantities and the methods for the preparation of the sorbents (in the course of their preparation, the ratio P/Zr varied from 1.2 to 1.9). Whereas for a high degree of reaction the equilibrium constant depends on the properties of the equilibrium phases, for a low degree of reaction it depends only on the nature of the active groups on the surface. Furthermore, for an equilibrium process there should be a possibility of attaining the final state from both the starting materials and from the final products. On the other hand, in the case of layered hydrogenphosphates of tetravalent elements, the reverse exchange frequently leads to the formation of compounds with a degree of hydration exceeding that for the initial substance and hence to a change in the equilibrium constant. Some investigators therefore do not believe at all that it is legitimate to employ the term 'equilibrium constant' for such quantities.

We shall now consider the factors that influence the thermodynamic parameters of ion exchange processes described by reaction (3). In the transfer of a cation A^{z+} with a radius R_A from a dilute solution to a singly charged ion-exchange group with a radius R_X , the electrostatic interaction energy

$$\Delta G = \frac{-z_A e^2}{R_A + R_X}, \quad (11)$$

is liberated and the hydration energy E_A is consumed. The change in energy on desorption of the cation B can be described similarly:

$$\Delta G = e^2 \left(\frac{z_B}{R_B + R_X} - \frac{z_A}{R_A + R_X} \right) + E_A - E_B. \quad (12)$$

Using this relation, Eisenman⁴⁰ has calculated series of the variation of the affinity of alkali metal cations for the sorbent as a function of R_X .

The relations presented 'work well' in the case of biological systems and ion-exchange resins on a polymer matrix. On the other hand, for inorganic sorbents their use is limited. This is due primarily to the fact that the concentration of the groups with the affinity for cations in such sorbents is high and the coordination sphere of the A^{z+} ion with a fixed distance between the ionogenic groups is formed in the ion exchanger matrix. The energy of the interaction of the cation with the ion exchanger matrix is found to be initially specified fully or partially (if a displacement of the cation in the coordination polyhedron is possible). It follows from simple geometrical calculations that, when the cation A^{z+} is localised at the centre of an octahedron made up of oxygen atoms in the interlayer space in the layered phosphates $A_X Y(PO_4)_2$ ($Y = \text{Ti, Zr, Hf, Sn, Pb, Sb, Ta}$), the distance $A-O$ may vary from 4.8–5.2 Å in the absence of distortion to 2.8–3.0 Å for the unlikely limiting model of a planar hexagon when the octahedron is compressed along the threefold axis. Evidently, the cavity formed is large for any cation. The affinity of the matrix for the alkali metal cation therefore increases with increase in the heat of hydration, *i.e.* with increase in the radius of the given cation. This can explain the increase in the selectivity of the sorption in the $\text{Li}^+ - \text{Cs}^+$ series. This type of effect is often abolished when part of the water is retained in the coordination spheres of the cations when the latter are incorporated in the ion exchanger matrix. The H_2O molecules also participate in the filling of the free volume.

The entropy of the sorption process may be determined as the difference between the entropies of the incoming and leaving groups in the sorbent and in the solution. The entropy is determined primarily by the change in the degree of hydration of the cations following their incorporation in the solid phase.³¹ The transfer of one water molecule from the ion exchanger to the solution at room temperature is on average accompanied by an increase in the entropy of the system by 25 kJ mol^{-1} . The insignificant tendency of large cations to be hydrated is responsible for the additional increase in the partition coefficients when the cations are sorbed in the anhydrous or weakly hydrated form.

III. Kinetics of ion exchange

In the study of the kinetics of ion exchange on polymeric matrices, diffusion within the grain, the migration of ions in a thin film surrounding the ion exchanger grain (the so-called film kinetics), and diffusion in the liquid phase, which may make an appreciable contribution only for dilute solutions, are usually considered as the main processes.⁴¹ In the study of ion exchange on inorganic sorbents, only the first two processes are considered, since the diffusion in solutions is significantly faster.

The quantitative description of diffusion processes of this kind is complicated by the following factors.

Firstly, it is extremely difficult to collect a fraction of crystals with a specified size. Secondly, the mutual diffusion coefficient (D_{AB}) of the exchanging ions varies during the process as the ratio of the mole fractions of the cations participating in the exchange (X_A and X_B) is varied:

$$\frac{1}{D_{AB}} = \frac{X_A}{D_A} + \frac{X_B}{D_B},$$

where D_A and D_B are the diffusion coefficients of the corresponding cations in the individual phases.⁴² Thirdly, there is a possibility of a change in the diffusion conditions in the solid matrix as a consequence of its transformation in the course of the exchange (for example, for layered phosphates as a consequence of the change in the interplanar spacings and in the degree of hydration).⁸ Fourthly, there is a possibility of a change in the size of the sorbent particles during the exchange process.^{43–45} The vast majority of studies have therefore been devoted to a qualitative description of the ion exchange kinetics.

The rate-limiting stage of the diffusion of cations in the solid phase is their passage through the common face of two coordination polyhedra within the crystal. As a result of the consecutive fusion of occupied and unoccupied polyhedra, conductivity channels appear and may extend in the structure along one, two, or three directions and hence ensure one-, two-, or three-dimensional diffusion. The size of the cross-section of such a channel is determined by the number of anion atoms constituting it and their nature. The required size may be estimated on the hypothesis of the close packing of the anions and of the formation by the latter of regular planar polygons in the cross-section (Fig. 3). The results of the calculation of the cross-sections formed by oxygen ions ($R = 1.40 \text{ \AA}$) are presented in Table 2. The size of the cross-sections of the channels may increase somewhat when account is taken of the radius of the polyvalent cations binding the oxygen atoms.

Cation	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺
Radius †	$\frac{0.59}{0.62}$	$\frac{0.99}{1.02}$	$\frac{1.37}{1.38}$	$\frac{—}{1.52}$	$\frac{—}{1.67}$

Furthermore, all the figures considered, starting with the tetragon, are nonrigid and the displacement of some of the ions from the plane of the channel cross-section leads to a decrease in their size.

Analysis of the data presented in Table 2 with allowance for the radii of the alkali metal cations makes it possible to conclude that the channels with a triangular cross-section are difficult to pass through by virtually all cations, while the channels with a tetragonal cross-section are difficult to pass through by all cations other than the lithium cation. The diffusion of the remaining cations requires at least pentagonal channels. However, it is known that lithium ions are capable of passing also through channels with a triangular cross-section made up of oxygen atoms.^{48,49} This ability is due to the activation energy for the given process.

In individual instances (for example, in polyphosphates of polyvalent elements), channels with a comparatively large cross-section are formed between oxygen atoms belonging to neighbouring planes, which facilitates the diffusion of cations. In order to ensure the diffusion of cations in $\alpha\text{-M}^{\text{IV}}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$, it is necessary that they should pass through the face of a coordination polyhedron with a radius of $1.3 \text{ \AA}$ made up of oxygen atoms.⁵⁰ Small cations (Li^+ , Na^+) permeate through it comparatively readily. For larger cations — with a radius $> 1.3 \text{ \AA}$ (K , Rb^+ , or

† The number above the line is the radius of a cation with a coordination number of 4, while the number under the line is the radius of a cation with a coordination number of 6.⁴⁷

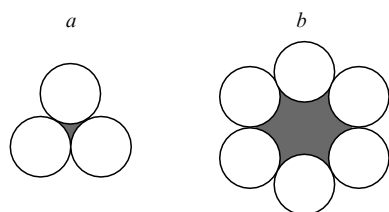


Figure 3. Schematic illustration of the formation of the triangular (a) and hexagonal (b) channels in the spherical close packing of oxygen atoms.

Table 2. Calculated radii of n -sided channels made up of oxygen atoms ($\text{\AA}$).

Packing of oxygen atoms	$n = 3$	4	5	6	$n = 8$
Close packing	0.22	0.58	0.98	1.40	2.26
Channels with planar E_nO_n rings ^a in zeolites ⁴⁶	0.25	0.45	0.75	1.1	1.9
Close packing of oxygen atoms separated by sum of their van der Waas radii	0.28	0.73	1.22	1.75	2.8

^a E = polyvalent cation.

Cs^+ for titanium phosphate and Rb^+ or Cs^+ for zirconium phosphate) — a considerable energy barrier must be overcome. In this case, for the implementation of the ion-exchange process it is necessary to maintain a high pH of the solution. The low activity of hydrogen ions is responsible for the possibility of the release of an additional number of protons from the ion-exchange material matrix. The latter acquires a negative charge and an electrostatic potential difference is created between the ion exchanger and the solution and is responsible for the diffusion of bulky cations into the cation exchanger. For this reason the exchange with lithium and sodium ions on $\alpha\text{-M}^{\text{IV}}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ takes place in acid solutions, while the exchange with caesium occurs only in alkaline solutions.^{33,50} In the case of $\gamma\text{-M}^{\text{IV}}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$ with a significantly greater interplanar spacing, the energy barrier is virtually absent and the exchange of all the cations occurs readily in acid solutions.³³ Strictly speaking, the determination of the equilibrium thermodynamic parameters of H^+/K^+ , H^+/Rb^+ , and H^+/Cs^+ exchange processes for the α -phosphates of tetravalent elements is difficult and the characteristics presented in Table 1 refer to the 'pseudo-equilibrium' state.

Alberti *et al.*⁵⁰ and Troup and Clearfield⁵¹ carried out the sorption of caesium ions on zirconium hydrogenphosphate in the presence of traces of sodium (Fig. 4). The cations of the latter substitute some of the protons on the surface of the crystals, as a result of which the interplanar spacing in the latter increase from 7.6 to $11.8 \text{ \AA}$. The gap between the planes for $[\text{M}^{\text{IV}}(\text{HPO}_4)_2]_n$ then expands and caesium cations enter freely into the lattice already at a pH close to 4.

In order to estimate the kinetic parameters of the ion-exchange processes, Barrer's method is used.^{52–54} The diffusion coefficients are calculated by means of the following equation:

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \frac{-D t \pi^2 n^2}{R^2}, \quad (13)$$

where F is the degree of completion of the exchange process, n an integer, D the diffusion coefficient, t the time, and R the radius of the ion-exchanger particles. The series in the equation quoted above converges comparatively rapidly for large values of F .

The diffusion coefficients calculated from the results of the ion-exchange experiments are presented in Table 3.

The above method has been used also to investigate ion-exchange processes on layered hydrogenphosphates of tetravalent elements. The diffusion coefficients and the activation energies for diffusion presented in Table 3 for these compounds differ markedly. The differences are due to the fact that the size of intergrown crystals and not the crystals themselves was used in a number of studies. In this case, an average diffusion coefficient was determined, since the rate of diffusion can be significantly different in the intergranular space and in the grain itself. On this basis, Larsen and Cilley³⁸ concluded that the values obtained are too high and they were unable to convert kinetic curves into diffusion coefficients.

Another problem is that Eqn (13) was derived by Barrer for a homogeneous isotropic spherical grain with a continuous series of solid solutions of the type $\text{A}_y\text{H}_{1-y}\text{X}$. On the other hand, none of the above conditions holds for many materials, among which one

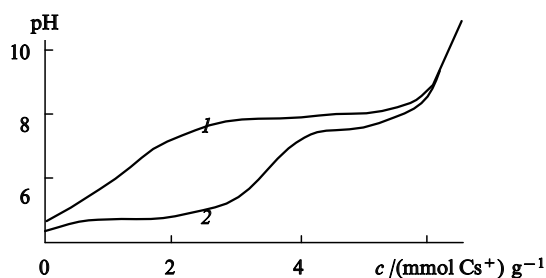


Figure 4. Curves for the titration of acid zirconium phosphate with caesium hydroxide in the presence of CsCl (1) and CsCl with added NaCl (2).

Table 3. Diffusion coefficients in certain inorganic ion-exchange materials calculated from experimental data.

Ions to be exchanged	$T/^{\circ}\text{C}$	$D/\text{cm}^2 \text{ s}^{-1}$	$E/\text{kJ mol}^{-1}$	Ref.
Basic cancrinite				
Na^+/Li^+	25 ^a	5.5×10^{-16}	56	55
Analcite				
Na^+/Ti^+	25 ^a	1.7×10^{-15}	62	56
Ultramarine				
Na^+/Ag^+	25 ^a	1.6×10^{-16}	94	55
Ag^+/Na^+	25 ^a	5.2×10^{-17}	92	55
Ag^+/Li^+	25 ^a	5.6×10^{-15}	113	55
Ag^+/K^+	75	5.7×10^{-16}	—	55
Na^+/Ag^+	25 ^a	7.2×10^{-16}	74	6
$\text{Na}^+/\text{Cu}^{2+}$	25 ^a	1.4×10^{-16}	87	6
$\text{Na}^+/\text{Co}^{2+}$	25 ^a	5.6×10^{-17}	93	6
$\text{Na}^+/\text{Ni}^{2+}$	25 ^a	8.1×10^{-17}	103	6
$\text{Na}^+/\text{Mn}^{2+}$	25 ^a	2.0×10^{-17}	99	6
Amberlite IR 1				
Na^+/Li^+	30	3.0×10^{-6}	—	55
Na^+/K^+	30	3.5×10^{-6}	—	55
$\alpha\text{-Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$				
H^+/Na^+	25	1.0×10^{-6}	—	6
H^+/Na^+	25	$(0.1-5) \times 10^{-11}$	—	57
H^+/Cs^+	25	1.1×10^{-8}	—	6
$\alpha\text{-Sn}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$				
H^+/Na^+	20	6×10^{-8}	31	37
H^+/K^+	20	5.3×10^{-8}	31	37
H^+/Cs^+	20	4.1×10^{-8}	46	37
$\alpha\text{-LiHTi}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$				
H^+/Li^+	20	8×10^{-12}	—	18
$\alpha\text{-NaHTi}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$				
H^+/Na^+	20	6×10^{-11}	—	18
$\alpha\text{-Li}_2\text{Ti}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$				
H^+/Li^+	20	2×10^{-13}	—	18
$\alpha\text{-Na}_2\text{Ti}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$				
H^+/Na^+	20	1×10^{-14}	—	18
$\alpha\text{-K}_2\text{Ti}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$				
H^+/K^+	20	1×10^{-13}	—	18
$\text{H}_5\text{O}_2\text{Ta}(\text{PO}_4)_2$				
H^+/Li^+	20	3.8×10^{-6}	26	58
$\text{Li}_{0.5}\text{H}_{0.5}\text{Ta}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$				
H^+/Li^+	20	1.1×10^{-6}	21	58
$\text{LiTa}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$				
H^+/Li^+	20	6.4×10^{-7}	20	58
$\text{Cu}_x\text{H}_{3-2x}(\text{PW}_{12})_{40} \cdot n\text{H}_2\text{O}$				
$\text{H}^+/\text{Cu}^{2+}$	25	6×10^{-8}	—	59

^a The literature data have been recalculated for 25 °C.

may identify also the layered hydrogenphosphates of tetravalent elements. The exchange in these substances takes place as a result

of the drift of the interface between the AX and HX phases with extremely narrow regions of homogeneity. The rate-limiting stage is then two-dimensional diffusion of A^+ and H^+ ions through the AX layer. In the latter case, one can therefore consider, as an alternative method for the study of ion exchange kinetics, the method of stationary concentrations where the pH of the solution is kept constant by adding an excess of alkali. The latter procedure is analogous to the method widely used in the description of topochemical solid-phase processes and is based on a simplified solution of the stationary diffusion equation

$$l^2 = Dt, \quad (14)$$

where l is the thickness of the substituted layer. The main disadvantages of this approach are the impossibility of taking into account the free energy of the exchange reaction, which determines the driving force of the diffusion process, and the probability of entering the region of nonstationary diffusion. Furthermore, the physical significance of the concept of 'the driving force of the diffusion process', believed as a rule to be the concentration gradient within the substance, is also lost. In compounds with a narrow region of homogeneity the concentration gradient is comparatively small.

The solution of the 'diffusion problem' for an ion exchange process occurring as a result of the migration of the interface between two phases, based on the consideration of the model of a species moving within the crystal in a field with a periodic potential and the chemical potential superimposed on it, has been examined by Yaroslavl'tsev and Khrulev.¹⁸ The chemical potential difference ($\Delta\mu$) between the solution and the interface in the crystal was chosen as the driving force of the process. The resulting kinetic equations for one-, two-, and three-dimensional diffusion through a plane, a hollow cylinder, and a hollow sphere assume the following forms respectively:

$$\frac{dQ}{dt} = Dc_0\Delta\mu \frac{S/l}{RT}, \quad (15)$$

$$\frac{dQ}{dt} = \frac{2\pi Dc_0 h \Delta\mu}{RT \ln(r_0/r)}, \quad (16)$$

$$\frac{dQ}{dt} = \frac{4\pi Dc_0 \Delta\mu [rr_0/(r_0 - r)]}{RT}, \quad (17)$$

where dQ/dt is the flux of diffusing ions, c_0 is the concentration of the migrating ions in the layer where diffusion takes place, S and l are respectively the area and thickness of the plate, h is the height of the cylinder, and r_0 and r are the outer and inner radii of the cylinder or sphere. The quantities l and r are variable and are determined by the thickness of the layer of the growing phase. In the course of the experiment, they can be determined from the amount of reagent added and its current concentration. The chemical potential difference between the interfaces can be found from the relation

$$\Delta\mu = RT \ln \frac{c_M c'_H}{c_H c'_M}, \quad (18)$$

where c and c' are respectively the equilibrium and current concentrations of the cations. The relations presented are valid also in the exchange for the large potassium, rubidium, and caesium cations. For these species, the passage of the interface between solid phases requires an additional chemical potential difference.¹⁸

IV. The main types of inorganic ion-exchange substances

Among inorganic ion-exchange compounds, it is possible to identify the following classes: complex oxides, globular hydrates, and salts of polyvalent elements.

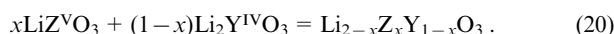
1. Complex oxides

Complex oxides are most widely represented among inorganic ion-exchange compounds. They include all natural ion exchangers — clay minerals and zeolites. The advantages of complex oxides is their availability and thermal and (partially) chemical stability. However, in view of the tendency of oxides to be close-packed, most of them have channels with small cross-sectional areas which must be passed by cations in order to migrate in the lattice. Furthermore, the high energy of the crystal lattices of the oxides is responsible also for the high energy of formation of defects in the latter (ΔH_f). As a consequence of this, the cationic diffusion coefficient is low and at room temperature does not as a rule exceed $10^{-10} \text{ cm}^2 \text{ s}^{-1}$.⁶⁰ The diffusion coefficient is defined by the relation

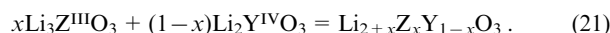
$$D = \frac{1}{6} f c a^2 v_0 \exp\left(\frac{\Delta S_f}{2R}\right) \exp\left(-\frac{E + \Delta H_f/2}{RT}\right), \quad (19)$$

where f is the correlation factor, which varies for the majority of substances from 0.33 to 0.78 as the coordination number of the cation increases, c is the concentration of the cations of the given type, a is the length of the elementary transfer step, v_0 is the pre-exponential factor for the transfer frequency in the range $10^{12} - 10^{14} \text{ s}^{-1}$, ΔS_f and ΔH_f are the entropy and enthalpy of the defect formation process, and E is the activation energy for the mobility of defects.

Calculations by Eqn (13) have shown that between three days and one year is required to achieve 95% completion of the exchange process for 0.1–1 mm oxide particles.⁶⁰ Such duration is characteristic of geological processes, but it cannot satisfy experimenters. A simple solution to this problem has been found: since the activation energy for diffusion in oxides is 80–100 kJ mol⁻¹, an increase in temperature by 100 °C leads, in conformity with Eqn (19), to an increase in the diffusion coefficient and hence in the rate of the process by 3–4 orders of magnitude. Bearing this in mind, the ion exchange, which occurs slowly at room temperature, is carried out either under hydrothermal conditions or in a melt.^{61,62} If this is insufficient and also if the thermal stability of the ion exchanger is low, experimenters attempt to reduce the enthalpy of formation of defects, for example by heterovalent doping. In particular, doping of $\text{Li}_2\text{Y}^{\text{IV}}\text{O}_3$ by a compound of a pentavalent element having the composition $\text{Li}_2\text{Z}^{\text{V}}\text{O}_3$ leads to formation of lithium vacancies in the structure:



On the other hand, doping with the compound $\text{Li}_3\text{Z}^{\text{III}}\text{O}_3$ leads to the appearance of interstitial lithium ions:



In materials of this kind, the energy of formation of defects is reduced to zero and the diffusion coefficient is defined by the relation

$$D = \frac{1}{12} f c x a^2 v_0 \exp\left(-\frac{E}{RT}\right). \quad (22)$$

Even for $x = 0.01$, the diffusion coefficient increases significantly and may prove to be fully acceptable for ion exchange at a comparatively low temperature.

a. Zeolites and clay minerals

Typical representatives of complex oxides with ion-exchange properties are zeolites and clay minerals. The structural base of these compounds consists of alternating layers of SiO_4 and AlO_4 tetrahedra or AlO_6 octahedra. The general formula of such compounds can be expressed in the form $\text{M}_{x/2}[(\text{AlO}_2)_x \cdot (\text{SiO}_2)_y] \cdot m\text{H}_2\text{O}$. All clay minerals have a layered structure and the blocks, approximately corresponding to the composition $\text{Si}_8\text{Al}_4\text{O}_{24}^{4-}$, are arranged at right angles to the crystallographic c

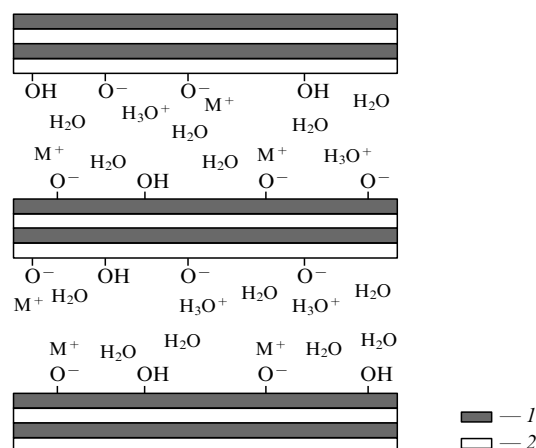


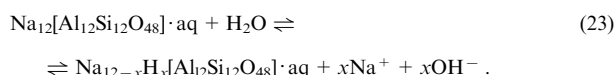
Figure 5. Schematic illustration of the structure of clay materials. (1) and (2) blocks of the layered structure; M^+ = alkali metal cation.

axis (Fig. 5). The surface of the blocks is made up of oxygen atoms carrying a non-compensated negative charge. The electroneutrality of the compound is ensured overall by the incorporation in the interstitial space of alkali or alkaline earth metal cations or protons,⁶ forming coordinate or valence bonds with the oxygen atoms of the $\text{Si}_8\text{Al}_4\text{O}_{24}^{4-}$ blocks. Some of these cations are capable of exchanging with the cations of the surrounding solution. The overall ion-exchange capacity of such materials ranges from hundredths to 1.5 mequiv g⁻¹ and for compounds with compositions close to $\text{H}_4\text{Si}_8\text{Al}_4\text{O}_{24} \cdot n\text{H}_2\text{O}$ the ion-exchange capacities with respect to cations and anions are approximately the same.⁶ A characteristic feature of such materials is their ability to swell in aqueous solutions or in water.

The silicon at tetrahedral sites can be partly substituted by aluminium cations, while aluminium at the octahedral sites can be substituted by a whole series of cations (divalent and trivalent iron, magnesium, and certain others with similar radii). Substitution by an ion with a smaller radius ($\text{Si}^{4+}/\text{Al}^{3+}$, $\text{Al}^{3+}/\text{Fe}^{2+}$, $\text{Al}^{3+}/\text{Mg}^{2+}$) increases the ion-exchange capacity with respect to cations. Therefore, for the majority of zeolites and clay minerals, the cation-exchange capacity exceeds the anion-exchange capacity. Clay minerals are distinguished by selectivity with respect to the sorption of large cations (Table 1). In the series of alkali metals, the selectivity increases from lithium to caesium.^{21,22,63,64}

In zeolites, the joining of the AlO_4 and SiO_4 tetrahedra *via* vertices, edges, or faces leads to the formation of diverse structures — fibrous, layered, or structures with a three-dimensional framework. The chemical and ion-exchange properties of zeolites with fibrous and layered structures are close to those of clay minerals, while those of zeolites having a rigid framework in the structure may differ significantly. The crystal lattices of the latter can be regarded to a first approximation as a $(\text{SiO}_2)_n$ matrix with three-dimensional connections, some of the silicon ions in which have been substituted by aluminium ions. The excess negative charge is compensated by the insertion into the lattice of cations with a smaller charge or by the substitution of some of the oxygen atoms by anions of monobasic acids. All these 'defective' cations and ions and also a certain number of water molecules are located within channels having different cross-sections (Table 2). If the size of the ions is smaller than the size of the channels, they can migrate in the structure and can participate in ion exchange. In contrast to clay minerals, the volume of such substances hardly changes during exchange and their ion-exchange capacity is determined by the chemical composition and may be fairly high. Thus, for certain minerals of the type of feldspar, it approaches 10 mequiv g⁻¹ (sodalite, ultramarine) or can actually exceed this

value (cancrinite).⁶⁵ Alkali metal cations are partly exchanged even on contact with water:



As a result of this, many zeolites in the initial form contain a certain number of protons.⁶⁶ In order to attain a more complete conversion into the hydrogen-form, zeolites are treated with solutions of ammonium salts at elevated temperatures, the ammonia formed being removed during annealing.^{67, 68}

Zeolites with a three-dimensional structure and a fixed size of the channels are used as 'ionic sieves'. Indeed, cations with a radius close to the radius of the cross-section of the channels are weakly sorbed, whilst still larger ones altogether fail to be sorbed. Thus ultramarine sorb effectively lithium, sodium, and silver ions and poorly rubidium and ammonium ions, while caesium does not participate in the exchange process.⁶⁵ Zeolites with a large size of the channels sorb weakly various alkylammonium cations,⁶ but certain zeolites are capable of sorbing even bulky complex cations.⁶⁹

The specific sorption properties of zeolites, their availability, low cost, and stability have led to their extensive practical application. For example, zeolites are used to extract heavy elements (including radioactive ones) such as caesium, thorium, and uranium from solutions.^{25, 63, 70–73} Zeolites modified with the aid of ion exchange by copper, nickel, platinum, ruthenium, and certain other cations are promising as catalysts in reactions involved in organic synthesis and for the conversion of nitrogen oxides and carbon monoxide in exhaust and industrial gases.^{74–82}

b. Complex oxides with a trivalent metal

Many complex oxides incorporating polyvalent elements have structures similar to those of the compounds examined above. The simplest representatives of complex oxides with a trivalent metal are alkali metal aluminates, chromates, and ferrites. The best known are the β -aluminates, also known as β -alumina having the composition $\text{M}_{1+x}\text{Al}_{11}\text{O}_{17+x/2}$ ($\text{M}^+ = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+, \text{H}_3\text{O}^+, \text{NH}_4^+, \text{Ag}^+, \text{Ti}^+, \text{etc.}$). These compounds are distinguished by a high ionic conductivity involving alkali metal cations or protons.^{83–85}

The structure of β -aluminates is made up of $\text{Al}_{11}\text{O}_{16}$ spinel blocks containing four layers with close packing of oxygen, each fifth layer containing only a quarter of the oxygen atoms retaining these blocks next to one another in crystals (Fig. 6). Alkali metal cations are located in the same layer, five cavities of different types corresponding to each. The population of cavities of each type depends not only on the nature of the singly charged cations but also on the stoichiometry of the compound and even on temperature.^{85, 86–90} β -Gallates also have a similar structure.^{91, 92} The extremely low energy barriers to jumps between the cavities (the

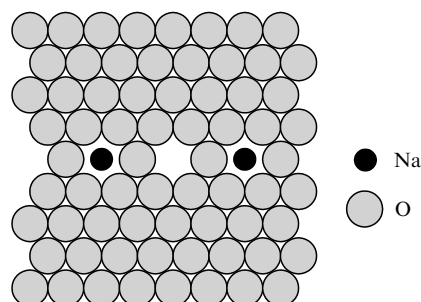


Figure 6. Schematic illustration of the structure of the oxygen sublattice of sodium β -aluminate with accommodation of the alkali metal cations in the conducting plane. The oxygen atoms in the conducting plane pass through the later.

minimum values correspond to silver and sodium ions) give rise to the possibility of rapid ion transfer. It is remarkable that, contrary to the generally accepted view, the similar energies for the localisation of singly-charged cations at different crystallographic sites, for example $(\text{NH}_4)_{1+x}\text{Al}_{11}\text{O}_{17+x/2}$, lead to a decrease in the population of the principal Beaver–Ross sites and to an anomalously rapid increase in the concentration of ammonia in the interstices with increase in the nonstoichiometry index x .⁹³ This fact can be explained by the displacement of ammonia from the main sites by the cations located in close proximity in the interstices.⁹⁴ Within the framework of the theory developed by Bruce and Abrahams,⁹⁵ such displacement leads to the formation of alternating structural blocks with populated sites and interstices and to the cooperative transport of ions. accordingly, nonstoichiometric compounds with a large value of $x^\ddagger$ are characterised by a high cationic mobility.^{96–100}

The first communication about the occurrence of ion exchange in sodium β -aluminates for alkaline earth metals is that of Toporov and Stukalova.¹⁰¹ Exchange of this kind occurs comparatively slowly at room temperature, but is significantly accelerated on raising it. It is therefore most suitable to carry out this process in nitrate melts at 300–350 °C.¹⁰² Under such conditions, the diffusion coefficient of even caesium β -aluminate reaches $10^{-7} \text{ cm}^2 \text{ s}^{-1}$ and the tendency of the structure to sorb cations increases in the sequence $\text{Ag}^+ > \text{Ti}^+ > \text{K}^+ > \text{Na}^+ > \text{Rb}^+ > \text{Li}^+ > \text{Cs}^+$.^{62, 102} The ammonium-forms of the β -aluminate^{62, 85, 99, 103} and β -gallate,^{98, 104, 105} as well as ammonium β -ferrite¹⁰⁶ can be obtained by exchange from the melt. In order to accelerate the removal of the alkali metal, the ammonium nitrate melt is electrolysed with a rubidium β -aluminate anode.¹⁰⁷ For the preparation of the oxonium forms of the β -aluminates, the exchange was carried out in inorganic acids at an elevated temperature^{105, 108–110} or the silver form of the β -aluminates was reduced with hydrogen.^{62, 111}

β -Aluminates are capable of sorbing multicharged cations, in particular the lanthanide cations.^{112–116} The latter are also localised in the conducting plane^{112, 113, 116} and are characterised by a comparatively high mobility.¹¹⁶

The α - NaCrO_2 -type structures of lithium and sodium ferrites and chromites consist of close-packed oxygen atoms, among which the alkali metal and chromium ions occupy alternately octahedral cavities in the direction of the (111) crystallographic planes.¹¹⁷ Interaction of these compounds with lithium and silver nitrate and copper(I) chloride melts leads to the formation of the compositions ABO_2 ($\text{A} = \text{Li}^+, \text{Ag}^+, \text{Cu}^+$; $\text{B} = \text{Fe}^{3+}, \text{Cr}^{3+}$).^{60, 118} When the corresponding process is carried out using a stoichiometric mixture of metallic palladium and palladium(II) chloride, the A sites may be occupied by palladium ions.¹¹⁸ Analogous reactions have been described also for a series of aluminates of monovalent and divalent metals.^{119, 120} When sodium chromite is treated with a 300-fold excess of 25% nitric acid for 12 h, it is possible to achieve virtually complete substitution of the sodium ions by protons.⁶⁰ It is noteworthy that not all the compounds obtained retain the crystal structure of the initial substance.

c. Complex oxides with tetravalent, pentavalent, and hexavalent cations

The layered titanates $\text{M}_2\text{Ti}_n\text{O}_{2n+1}$ and $\text{M}_4\text{Ti}_n\text{O}_{2n+2}$, the structures of which are made up of $\text{Ti}_n\text{O}_{2n+1}^-$ or $\text{Ti}_n\text{O}_{2n+2}^{2-}$ layers, are inorganic ion-exchange materials. On being combined *via* common edges or vertices, the TiO_6 octahedra form infinite cavities between which alkali or alkaline earth metal cations are located.^{121–130} Since the latter possess a fairly high mobility, they can be substituted in solutions or melts by M^+ and M^{2+} cations or protons. A certain number of water molecules, can also

[‡] Such compounds are frequently referred to as β'' -aluminates (gallates, ferrites).

permeate into the interlayer space.^{60, 126, 128, 130, 131} The exchange reactions in these compounds may prove to be hindered kinetically. Thus treatment of lithium titanate with a zinc chloride melt leads to only partial exchange.⁶⁰ This phenomenon can be explained by postulating that the cationic sites are nonequivalent: only some of them are capable of being substituted by zinc cations, as in lithium germanates described by Joubert and Durif.¹³² A series of new titanates have also been synthesised in recent years, among which one may differentiate fibrous materials containing hydrogen or alkali metal cations within $\text{Ti}_8\text{O}_{18}^{4-}$ layers and octahedral $\text{Ti}_8\text{O}_{17}^-$ tunnels. The cations within the layers tend to exchange rapidly, while those located within the tunnels are inert.¹³³

One of the few representatives of hydrated oxides of polyvalent cations, capable of stoichiometric ion exchange, is polyantimonic acid $(\text{H}_3\text{O})_2\text{Sb}_2\text{O}_6 \cdot \text{H}_2\text{O}$. Together with the method usually employed for the synthesis of hydroxides, namely deposition from solution, this acid can be obtained with the aid of the ion-exchange reaction occurring on treatment of potassium antimonate with nitric acid.¹³⁴ The compound formed has the pyrochlore structure with oxonium ions in the octahedral cavities.^{134, 135} The protons of polyantimonic acid are capable of being quantitatively substituted by alkali metal cations. The selectivity series then assumes the following form: $\text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+ > \text{Li}^+$, while the overall ion-exchange capacity reaches $5.1 \text{ mequiv g}^{-1}$.^{136–139}

Alkali metal niobates and tantalates (pyrochlore structural type) are also capable of undergoing stoichiometric substitution of all the cations by hydrogen. The ion-exchange capacities of these compounds reach $2\text{--}3.3 \text{ mequiv g}^{-1}$. This is due to the appreciable polarisation of the oxygen ions, leading to the formation of weak bonds between the lattice and the exchanging cation and to the presence of comparatively large channels. The hydrogen-forms of these ion exchangers may be obtained as a result of the hydrolysis of the pentachlorides⁸ or by the acid treatment of thallium,^{134, 140} lithium,^{141–145} or potassium¹⁴⁶ niobates at an elevated temperature. In contrast to antimononic acid, only half of the $(\text{H}_3\text{O})\text{HM}_2\text{O}_6$ protons are hydrated in niobium and tantalum hydroxides. NMR data have also confirmed the presence of protons and oxonium ions in these substances.¹³⁴ Many investigators have concentrated particular attention on the study of the phases formed at intermediate stages of the exchange process.^{142, 143, 145}

In order to obtain ion-exchange materials with a high capacity and high rates of exchange, it appears attractive to synthesise compounds with heterovalent substitution of the atoms in the ion-exchanger matrix. A considerable number of studies have been devoted to the preparation of mixed titanates, niobates, and tantalates with a layered or tunnel structure. The best known are the compounds $\text{MTi}_n\text{NbO}_{2n+3}$, and $\text{M}_3\text{Ti}_n\text{NbO}_{2n+4}$.^{147–153} The monovalent cations in these substances ensure a charge balance in the structure, remaining weakly bound to the framework. The alternating TiO_6 and NbO_6 octahedra, joined together by common edges or vertices, form double layers between which singly charged cations, capable of being substituted, are located.¹⁵² The reactivities of mixed titanates - niobates differ significantly. Thus the substitution of the alkali metal cation for a proton in MTiNbO_5 takes place comparatively easily, while the analogous process involving $\text{CsTi}_2\text{NbO}_7$ requires treatment with concentrated acid and the reaction product is the hydrate $\text{HTi}_2\text{NbO}_7 \cdot 2\text{H}_2\text{O}$. In the case of $\text{K}_3\text{Ti}_5\text{NbO}_{14}$, the maximum degree of substitution of potassium by hydrogen reaches only 80%.^{148, 152}

Variable-composition compounds, incorporating singly, doubly, triply, and quintuply charged cations together with titanium, may be differentiated as a separate group. The formulae of such compounds can be written as $\text{A}_x^I\text{B}_x^{II}\text{Ti}_{2-x}\text{O}_4$, $\text{A}_x^I\text{B}_x^{III}\text{Ti}_{2-x}\text{O}_4$, and $\text{A}_{1-x}\text{Ti}_{1-x}\text{Nb}_{1+x}\text{O}_5$.^{148, 151, 154, 155} In the compounds of the first two types, the substitution of part of the titanium by atoms B with a lower valence leads to a deficiency of cations, which is compensated when the corresponding number of ions A^+ are inserted into

the interstices. On the other hand, in compounds of the third type the compensation of the charge on substitution of titanium by niobium leads to the formation of vacancies in the cationic sublattice. Such a defective structure is distinguished by an increased cationic mobility, which helps to accelerate ion-exchange processes. On the other hand, the ion exchange of caesium for lithium, sodium, or potassium in $\text{Cs}_{0.7}\text{Mg}_{0.35}\text{Ti}_{1.65}\text{O}_4$ proceeds comparatively rapidly in melts at $300\text{--}400^\circ\text{C}$. However, the completion of the exchange of caesium for sodium in an aqueous solution requires four days.¹⁵⁵

Heterovalent substitution is possible in niobates and tantalates. The layered niobates and tantalates containing calcium or lanthanum were investigated vigorously in the 1980s–1990s.^{156–162} Treatment of these compounds with concentrated acids at 60°C leads to fairly rapid ion exchange.^{157, 159} The proton conductivity of the hydrogen-form of a series of such materials reaches $10^{-3} \text{ S cm}^{-1}$ at 400°C .¹⁶² Certain compounds containing niobium or tantalum together with tungsten or molybdenum also possess similar properties.^{163–165} The complete substitution of potassium by hydrogen on treatment with concentrated hydrochloric acid even of the stoichiometric compound KTaWO_6 occurs at room temperature. The hydrate $\text{HTaWO}_6 \cdot \text{H}_2\text{O}$ formed exhibits an appreciable proton conductivity of $2 \times 10^{-7} \text{ S cm}^{-1}$ at 25°C .¹⁶⁵

d. Oxides with variable-valence cations

An effect analogous to heterovalent doping may be obtained on partial oxidation or reduction of the ions of the framework. A typical representative of sorbents with a variable valence of the lattice cations is manganese dioxide. It has long been noted that the freshly precipitated compound contains an appreciable amount of impurity ions which can be readily exchanged for cations present in the solution surrounding it.^{166, 167} This is due to the fact that manganese dioxide contains divalent and trivalent manganese. Its composition may be represented by the formulae $\text{Mn}_n^{II}\text{Mn}_y^{III}\text{Mn}_{1-x-y}\text{O}_{2-2x-y}(\text{OH})_{2x+y} \cdot m\text{H}_2\text{O}$ or $\text{MnO}_{2-x}(\text{OH})_x \cdot n\text{H}_2\text{O}$ (the charge is compensated as a result of the insertion of protons, which form OH groups with oxygen). It was initially postulated that only hydroxy groups located on the surface of the particles of the test substance, may participate in the exchange process. However, it was later shown that the ion-exchange capacity of manganese dioxide may reach 4 mequiv g^{-1} ,^{168, 169} which in no way agrees with this hypothesis. All the known modifications of manganese dioxide are made up of MnO_6 octahedra joined together in such a way that long channels are formed between them.⁸ Singly and doubly charged cations are in fact located within these channels and readily migrate along them, ensuring the possibility of exchange processes.

Among other compounds with distinct ion-exchange properties, one may identify the tungsten and molybdenum blues and bronzes A_x^IBO_3 , which possess both electronic and ionic conductivity. They can be readily obtained by the electro-chemical reduction of molybdenum or tungsten oxides and also by the interaction of the latter with the corresponding metal or hydrogen at an elevated temperature. Vanadium and niobium bronzes possess similar properties. In the simplest case, small cations are intercalated in the octahedral cavities of the tungsten or molybdenum oxide lattice. The formation of tunnel or layered structures is an alternative.¹⁷⁰ All these compounds have been thoroughly described in the literature, but they are not often used for ion-exchange processes. Therefore, without dealing in detail with their properties, we shall note only some of the latest studies where these compounds were examined.^{171–173}

2. Globular hydrates

Globular hydrates are widely distributed compounds, typical representatives of which are loose deposits of hydrated oxides of polyvalent elements of the type $\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ and $\text{ZrO}_2 \cdot n\text{H}_2\text{O}$. Since such compounds are sparingly soluble, their formation reactions occur at a high degree of supersaturation of the solutions

where the rate of nucleation is very high and fully comparable to the rate of growth of the particles. The precipitated deposits represent a large number of very small and poorly formed (amorphous or weakly crystallised) particles. The geometry of small particles is in many respects determined by the requirement that the surface tension energy be minimised.⁹⁴ The formation of particles in the form of spheres (globules), the core of which usually has a composition close to that of the corresponding oxides is the most favourable. The extensive surface of the globules contains a multiplicity of uncompensated bonds, which may be stabilised as a result of the sorption of protons H^+ and OH^- groups from the solution,¹³⁶ as well as other ions and water molecules (Fig. 7a). The bonds between the sorbed particles and the core are comparatively weak, so that dissociation of the $\equiv E-O-H$ groups *via* an acid or base mechanism and the transfer of the resulting ions into the intergranular space are possible.¹³⁶

The most significant difference between the globular hydrates and the substances described above is the variable and comparatively low ion-exchange capacity determined in the first place by their surface area. After prolonged storage or heating, particularly under hydrothermal conditions, olation, oxolation, and crystallisation processes involving the substances take place,¹⁷⁴ as a result of which the ion-exchange capacity may decrease by several orders of magnitude. Furthermore, we may recall that the ion-exchange capacity depends significantly on the pH of the solution in contact with the hydroxides^{12,13} and even the nature of the process occurring on raising the pH changes from anion-

exchange to cation-exchange reactions. Since the nature of the active centres on the surfaces of globular hydrates depends on the method of their preparation, the position of the equivalence point is not a fundamental characteristic of the substance but depends on its previous history. Nevertheless the relation between cation- and anion-exchange properties of hydrated oxides is determined primarily by the electronegativity of the polyvalent cation. Thus the distinctly acid hydrated antimony(V) oxide, mentioned above, may participate only in cation exchange.¹³⁶ On the other hand, the hydrated yttrium oxide, dissociating preferentially *via* a basic mechanism, is an anion exchanger.²⁰

The presence of ion-exchange properties in globular hydrates may lead to their contamination and hence to an ambiguous treatment of the experimental results. For example, the hydroxides of trivalent elements are most often obtained by deposition with ammonia from solutions of salts of the corresponding metals. The deposition product is characterised by an appreciable content of the anions of the initial salts. This is due to the fact that the resulting solution is a buffer containing the $NH_4X + NH_4OH$ mixture.²⁰ The concentration of hydroxide ions in it in the presence of a 10% excess of the precipitant reaches only 2×10^{-6} and is several orders of magnitude lower than the concentration of the anions X^- . For this reason, the surface of the globules actively sorbs the anions. The content of nitrate ions in the yttrium hydroxide $Y(OH)_{3-x}(NO_3)_x \cdot 0.7H_2O$ ($0 < x < 0.5$), obtained by deposition from a nitrate solution, corresponds to the fraction of the cations localised on the surface of the particles.²⁰ For the complete conversion of the compounds thus obtained into the hydroxide, it is necessary to wash them with solutions of alkalis containing OH^- ions. Similar ion-exchange processes may occur also on much better formed deposits, for example on hydrated aluminium oxide.^{173,176}

Materials with distinct anion-exchange properties may be obtained by doping hydrated oxides having basic properties with an admixture containing a high-valence cation. It has been postulated^{6,177} that the excess positive charge is compensated as a result of the sorption of anions from the $Zn_{1-y}Al_y(OH)_2X_y$ solution. However, this interpretation appears doubtful, since the initial hydroxide already possesses similar properties and is characterised by a significant degree of disorder, which should abolish the effect of heterovalent doping.

Among globular hydrates, hydrated oxides of tetravalent elements (silicon, tin, titanium, and zirconium) are most often employed as ion-exchange materials. Their principal advantage is very low solubility in both acid and alkaline solutions. In the series of compounds quoted, the acid properties are somewhat weakened:¹³⁶ whereas silicon hydroxide can participate only in cation exchange, for the zirconium compound the zero-charge point is attained at a pH close to 7.^{12,13,176,178,179} Dichromate and molybdate ions are sorbed in the anionic form, the latter being involved in octahedral coordination, which does not rule out the possibility of the condensation of polyanions on the surface of the hydroxides.¹⁷⁹ Hydrated vanadium(V) oxide also has properties close to those of the compounds listed above.^{136,180}

A series of specific properties of hydrated oxides are determined by the characteristics of their structure. In the first place, such properties are determined by the nature of the highly mobile 'solution' in the interlayer space, which contains water molecules and ions formed on dissociation of the groups localised on the surface. In view of the extremely small size of the micropores ($< 100 \text{ \AA}$ ¹⁸¹) containing the intergranular solution and also as a consequence of the lack of order in the system of hydrogen bonds formed within it and on the surface of the globule, such a solution has a very high mobility. The latter vanishes only on cooling the specimen to temperatures close to the boiling point of nitrogen.^{178,181-183} The presence of proton defects (H_3O^+ or HO^-) in the solution is responsible for a fairly high proton conductivity of globular hydrates, the magnitude of which reaches $10^{-2} \text{ S cm}^{-1}$ for the series of compounds (Table 4). The proton conductivity and the mobility of the proton-containing groups decrease sig-

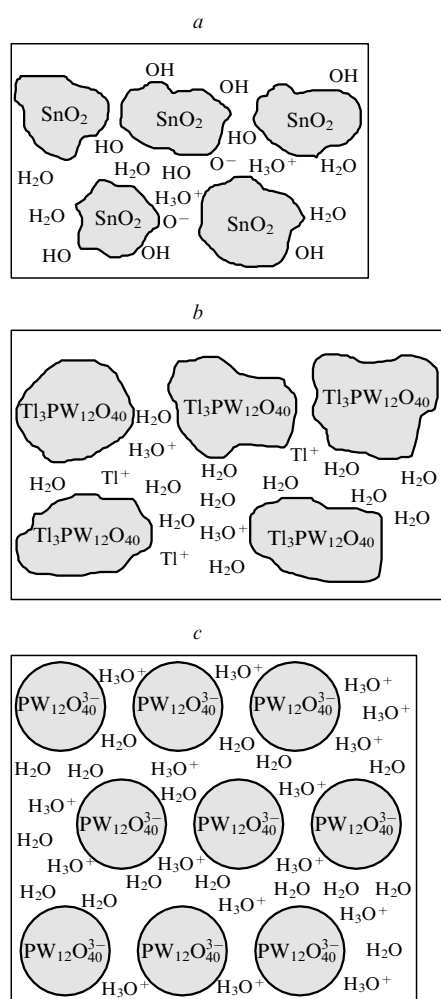


Figure 7. Schematic illustration of the structures of the globular hydrates $SnO_2 \cdot nH_2O$ (a), $Tl_{3-x}H_x(PW_{12}O_{40}) \cdot nH_2O$ (b), and $H_3PW_{12}O_{40} \cdot 29H_2O$ (c).

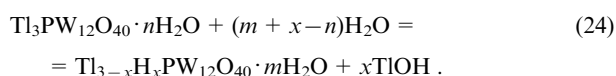
Table 4. The proton conductivities of certain globular hydrates.

Oxide or heteropolyacid	Extent of solvation	$\sigma_{298\text{ K}}$ /S cm ⁻¹	Ref.
Ga ₂ O ₃	4H ₂ O	10 ⁻⁴	184
Cr ₂ O ₃	8.5H ₂ O	10 ⁻⁵	184
In ₂ O ₃	5–6 H ₂ O	(1–3) × 10 ⁻³	184
ZrO ₂	1.7–5.6 H ₂ O	10 ⁻⁴ –10 ⁻⁵	136
SnO ₂	2–3 H ₂ O	(2–4) × 10 ⁻⁴	136
CeO ₂	2H ₂ O	10 ⁻⁵ –10 ⁻⁶	185
ThO ₂	3–5 H ₂ O	5 × 10 ⁻⁶ –4 × 10 ⁻⁴	184
V ₂ O ₅	0.5–1.8 H ₂ O	10 ⁻⁴ –10 ⁻²	185, 186
Sb ₂ O ₅	0.6–6.5 H ₂ O	10 ⁻⁴ –3 × 10 ⁻³	134, 184, 187, 188
Nb ₂ O ₅	0.3–0.8 H ₂ O	10 ⁻⁴	134
Ta ₂ O ₅	0.5–1 H ₂ O	10 ⁻⁴	134
H ₃ PMo ₁₂ O ₄₀	6–29 H ₂ O	7 × 10 ⁻⁵ –0.17	189, 191
H ₃ PW ₁₂ O ₄₀	6–29 H ₂ O	8 × 10 ⁻⁴ –8 × 10 ⁻²	191–193
	6CH ₃ OH	4.5–10 ⁻⁴	193
	6CH ₃ CN	1.8 × 10 ⁻⁵	193
	6C ₂ H ₅ OH	10 ⁻⁴	193
	6(CH ₃) ₂ CO	8 × 10 ⁻⁶	193
	6CH ₃ COC ₂ H ₅	5 × 10 ⁻⁶	193
	6(CH ₃) ₂ SO	2 × 10 ⁻⁷	193

nificantly during the dehydration of the hydrated oxides.^{136, 182, 184} The kinetics of the exchange processes depend on the relative permittivity of the solvent, since ion-exchange processes take place on the surface of the particles of the globular hydrates and in the intergranular solution. The rate of exchange and the capacity of the ion exchanger may therefore change, for example in the presence of alcohols.¹⁹⁴

Alkali metal and thallium tungstophosphates, the ion-exchange properties of which have been examined by Yaroslavtsev *et al.*,^{195, 196} are constructed similarly. The X-ray diffraction patterns of these compounds are identical with those of the anhydrous salts of the heteropolyacids constituting the cores of the globules, but differ by the broadening of the reflections corresponding to the formation of 80–200 Å particles. Water molecules are localised in the inter-granular space (Fig. 7b), their number varying from 7 to 12 per formula unit. In the interaction of solutions of heteropolyacids and alkali metal chlorides, a high concentration of hydrogen ions is maintained. For this reason, not only alkali metal cations but also protons are sorbed on the particles deposited from the solution. In the presence of an excess of the chloride, the trisubstituted salts M₃PW₁₂O₄₀·*n*H₂O are deposited, their formation being thermodynamically most favourable. In the presence of a deficiency of the chloride, their surface sorbs heteropolyanions and protons, which is equivalent to the deposition of acid salts in which the content of hydrogen ions may reach 1.05 per formula unit (for example, Cs_{1.95}H_{1.05}PW₁₂O₄₀·*n*H₂O characterised by a minimal solubility product and a minimal crystal size).¹⁹⁵

It has been established by ²⁰⁵Tl NMR that a significant proportion of the thallium ions in Tl₃PW₁₂O₄₀·11.5H₂O are in a mobile state.¹⁹⁶ Prolonged washing of the above compound with water leads to the disappearance of the line due to mobile thallium, which indicates its removal from the surface of the globules as a result of the reaction



The process described above leads to an increase in the ionic conductivity from 2.7 × 10⁻⁴ to 5 × 10⁻⁴ S cm⁻¹ in view of the greater mobility of protons compared with Tl⁺ ions.¹⁹⁶ The increase in ionic conductivity on passing from neutral to acid salts of heteropolyacids has been noted also for other cations.^{195, 197}

From the standpoint of thermodynamics, the formation of particles smaller than 100 Å is difficult owing to the considerable expenditure of energy on the formation of the interface. There is therefore probably a limiting minimum size of the hydrate globules. However, the series of compounds examined is aptly supplemented by the hydrates of heteropolyacids with a high water content (H₃PX₁₂O₄₀·29H₂O, where X = Mo, W), the anion of which, with a radius of ~12 Å, can be regarded as a micro-globule (Fig. 7c).¹⁹⁸ The high mobility of the 'intergranular' 3H⁺·29H₂O solution disappears at very low temperatures.⁵⁹ The proton conductivity of these compounds is a maximum among all those measured at room temperature,¹⁹⁰ its magnitude decreasing significantly in the course of dehydration (Table 4). Similar properties are characteristic of numerous heteropolyacid solvates.¹⁹³ The conductivity of such solvates diminishes with increase in the volume of the solvent molecule (in conformity with the decrease in its rotational mobility, which is required for the transfer of a proton).

It is difficult to observe ion exchange for heteropolyacid hydrates because their crystal lattice is unstable and readily disintegrates on contact with the solvent. Nevertheless, an ion-exchange process was achieved when H₃PW₁₂O₄₀·29H₂O and Cu_{3/2}PW₁₂O₄₀·28H₂O single crystals came into contact.⁵⁹ The mutual diffusion of copper and hydrogen ions can be observed readily in this case from the change in the colour of the crystals. The coefficient of the mutual diffusion of H⁺ and Cu²⁺ is (3–7) × 10⁻⁸ cm² s⁻¹.

There are no fundamental differences between the structure of globular hydrates and that of the hydrated antimony and manganese oxides described above. However, the microstructures of the cores of the globules and the chemical individuality of the polyvalent cation in the latter determine the possibility of the occurrence of exchange processes throughout the bulk of the particles, which in fact serves as the basis for their assignment to the class of complex oxides. On the other hand, from the standpoint of the interpretation of the nature of the proton conductivity, all these compounds can be assigned to globular hydrates, because the conductivity within the grain is negligible compared with the surface component. The use of fractal geometry appears extremely productive in the treatment of the properties of compounds with a high surface area and porosity.¹⁹⁹

3. Salts of polyvalent elements

a. The layered hydrogenphosphates and arsenates H₃B(XO₄)₂

Among the salts of polyvalent elements, the sparingly soluble phosphates and arsenates H₃B(XO₄)₂ are most widely used as inorganic ion-exchange materials. Zirconium hydrogenphosphate Zr(HPO₄)₂·*n*H₂O has been undoubtedly most thoroughly investigated. Investigators have shown particular interest in this compound after a communication had been published in 1943 concerning the possibility of separating with its aid uranium and plutonium from their fission products.²⁰⁰ The communication of Clearfield and Stynes⁵ about the synthesis of crystalline zirconium hydrogenphosphate stimulated the development of research into the nature of ion exchange on inorganic phosphates.

Zirconium hydrogenphosphate may be obtained after prolonged heating of a mixture of zirconium oxychloride with an excess of phosphoric acid or by evaporating the corresponding solution with added hydrofluoric acid. In this case, the slow disintegration of zirconium fluoride complexes results in the deposition of well formed Zr(HPO₄)₂·H₂O crystals. The latter consist of long [Zr(HPO₄)₂]_n layers, in which zirconium ions are in an octahedral environment consisting of the oxygen atoms of the anions (Fig. 8). Only three oxygen atoms of the anion participate in the formation of the P–O–Zr linkages, while the fourth is oriented towards the interplanar space and is linked to hydrogen *via* a valence bond. The layers are retained next to one another *via* hydrogen bonds with water molecules (O₃PO–H–OH₂) 2.77 and 2.81 Å long.^{50, 201} The acid nature of the HPO₄²⁻ groups and the nearly optimum lengths of the hydrogen bonds²⁰² create precon-

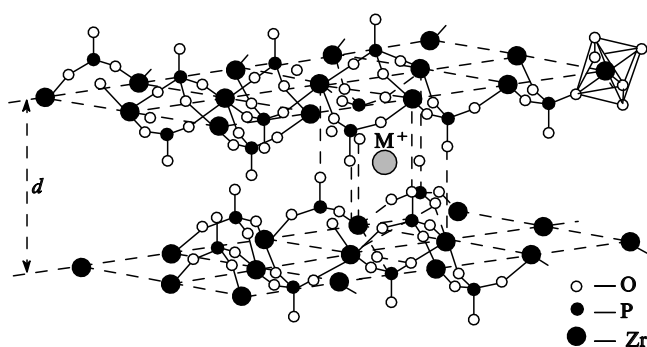


Figure 8. A fragment of the structure of acid zirconium phosphate with an indication of the preferred site where the cation is located in the distorted octahedron made up of oxygen atoms.

ditions for the appearance of proton conductivity in $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ and, together with the possible cationic diffusion in the interlayer space, for the appearance of ion-exchange properties.

A considerable number of hydrogenphosphates of polyvalent elements are isostructural with the above compound, but, in view of the difficulty of obtaining large crystals, structural data are available only for a few of them.^{203, 204} The main characteristics of these materials are the interlayer distance and the ion-exchange capacity (Table 5).

A new phase — $\alpha\text{-Zr}(\text{HPO}_4)_2 \cdot 0.5\text{H}_2\text{O}$ with an interlayer distance of 7.42 Å — has been described and characterised

Table 5. Interlayer distances and calculated ion-exchange capacities of certain acid phosphates and arsenates of tetravalent elements.

Composition	Interlayer distance /Å	Ion-exchange capacity /mequiv g ⁻¹	Ref.
$\alpha\text{-Ti}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$	7.60	7.75	203
$\alpha\text{-Ge}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$	7.71	7.08	205
$\alpha\text{-Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$	7.56	6.64	50, 201, 206
$\alpha\text{-Sn}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$	7.87	6.09	207
$\alpha\text{-Hf}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$	7.58	5.15	204
$\alpha\text{-Pb}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$	7.95	4.79	205
$\alpha\text{-Ti}(\text{HAsO}_4)_2 \cdot \text{H}_2\text{O}$	7.78	5.78	205
$\alpha\text{-Ge}(\text{HAsO}_4)_2 \cdot \text{H}_2\text{O}$	7.86	5.40	205
$\alpha\text{-Zr}(\text{HAsO}_4)_2 \cdot \text{H}_2\text{O}$	7.74	5.14	205
$\alpha\text{-Sn}(\text{HAsO}_4)_2 \cdot \text{H}_2\text{O}$	7.89	4.80	205
$\alpha\text{-Hf}(\text{HAsO}_4)_2 \cdot \text{H}_2\text{O}$	7.79	4.20	205
$\alpha\text{-Pb}(\text{HAsO}_4)_2 \cdot \text{H}_2\text{O}$	7.97	3.96	205
$\gamma\text{-Ti}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$	11.62	7.24	208, 209
$\gamma\text{-Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$	12.25	6.27	210
$\text{H}_5\text{O}_2\text{Ta}(\text{PO}_4)_2$	9.50	2.02	211, 212

structurally comparatively recently.²¹³ It differs from the monohydrate by the system of hydrogen bonds. The authors²¹³ note the stability of this phase — they did not observe its conversion into a mixture of the monohydrate and the anhydrous compound.

The interlayer distance in the γ -modifications of the acid phosphates $\gamma\text{-M}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$ is significantly greater^{208–210} than in the α -modification, which facilitates the occurrence of ion-exchange processes. The study of the structure of compounds of this type is complicated because only finely disperse specimens are obtained in the course of synthesis. For this reason, none of the information concerning their structure can be regarded as fully reliable. However, it has been established reliably with the aid of ³¹P NMR that two nonequivalent PO_4 polyhedra, coordinated twice and four times to the multicharged cation, are present in the

structure.²¹⁴ As a result of this, the H_2PO_4^- anions are displaced into the interlayer space, which in fact leads to the layers moving apart (Table 5).

Tantalum hydrogenphosphate has a structure similar to that of the α -phosphates of tetravalent elements.^{211, 212} However, the number of hydrogen ions in this compound is smaller by a factor of 2 and the negative charge of the basic layers is therefore smaller, the interaction between them is weaker, and the interlayer distance is greater.²¹² Furthermore, the polarisation of the phosphate anion by the pentavalent cation decreases the proton-accepting capacity of the oxygen atoms and leads to the dissociation of the HPO_4^- groups giving rise to diaquahydrogen ions H_5O_2^+ .²¹²

In the course of ion exchange on α -phosphates, alkali metal cations permeate into the interlayer space and are disposed in the vicinity of the centre of the octahedron made up of the oxygen atoms of the anion (Fig. 8) not coordinated to the tetravalent cation. A type $\text{AB}(\text{XO}_4)_2$ lattice with the structure of an anhydrous alum is obtained. Numerous double antimony and tantalum phosphates with alkali metals are constructed in this way.^{215–218} The coordination sphere of potassium in zirconium phosphate with a degree of substitution of 50% [$\text{ZrKH}(\text{PO}_4)_2$] is formed similarly.²¹⁹ The real radius of the octahedral cavities in such structures is equal to 4.7–5.3 Å and the radius of the cation in it should be 3.3–3.9 Å, which exceeds significantly the size of any alkali metal cation. The above octahedra therefore contract along the threefold axis and the interlayer distance diminishes. However, this contraction is insufficient and the excess space is filled with water molecules. The cation then shifts from the highly symmetrical position and the interlayer distance increases as a rule relative to that in the initial acid phosphate.³⁹

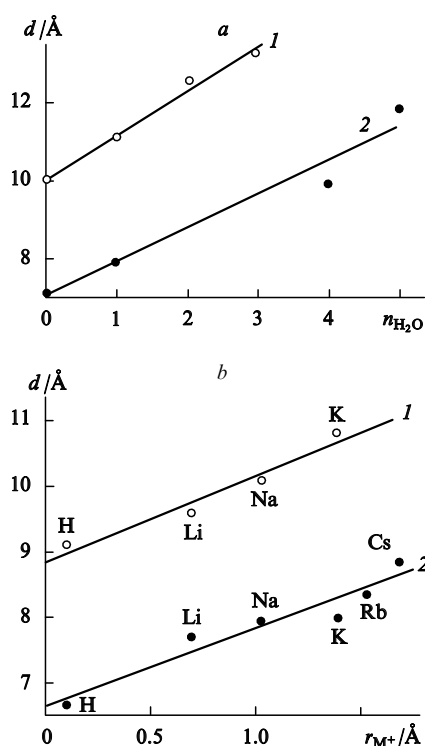
The number of highly symmetrical sites at the centre of the octahedron is smaller by a factor of 2 than the number of monovalent cations in the structure of the products of the complete substitution of tetravalent elements in acid phosphates. As a result of this, the coordination sphere of the metal is formed in a specific manner — with partial involvement of the oxygen atoms of the anion and water molecules. Thus there are four nonequivalent cationic sites in $\text{Na}_2\text{Zr}(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ with coordination numbers of 7, 7, 6, and 4. Between one and four water molecules and between two and five oxygen atoms of the anion enter into the immediate environment of sodium. Among the oxygen atoms, there are also those involved in the formation of P–O–Zr linkages.²²⁰ In $(\text{NH}_4)_2\text{Zr}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, two nonequivalent types of ammonium ions are surrounded by respectively four and five oxygen atoms of the anion and are linked to a water molecule *via* a bridging hydrogen bond: $\text{NH}_4^+ - \text{HOH} - \text{NH}_4^+$.²²¹

During ion exchange on acid phosphates, the structure of the $[\text{M}(\text{PO}_4)_2]_n$ layers is kept almost constant. Therefore, when the unit cell parameters a and b are similar, the interlayer distance changes significantly (usually increases), which is a sign of the occurrence of ion-exchange processes for the compounds $\text{M}(\text{HXO}_4)_2 \cdot \text{H}_2\text{O}$. The typical interlayer distances in certain products of ion exchange on acid phosphates with the ratio $\text{M}:\text{XO}_4 = 1:2$ are presented in Table 6 and their dependences on the degree of hydration and the radius of the cation in the monosubstituted sodium salts of zirconium α -phosphate and titanium γ -phosphate are shown in Fig. 9. The interlayer distance increases with increase in the radius of the sorbed cation and with the degree of hydration of the compound.

As a consequence of the structural nonequivalence of the hydrogen atoms in the hydrogenphosphates of tetravalent elements and the steric hindrance to the accommodation of a second cation, the exchange process on α -phosphates usually occurs in two stages. There is therefore a possibility of the formation of two substitution products — $\alpha\text{-AHM}(\text{HXO}_4)_2 \cdot n\text{H}_2\text{O}$ and $\alpha\text{-A}_2\text{M} \cdot (\text{HXO}_4)_2 \cdot n\text{H}_2\text{O}$, where A is an alkali metal cation. The formation of only the product of the complete substitution of protons has been noted for large cations. It has been shown^{18, 50} for potassium, rubidium, and caesium ions that this is caused by the kinetic inhibition of the exchange process. After the substitution of the

Table 6. Degrees of hydration (n) and interlayer distances (d) in the products of ion exchange on acid phosphates with the ratio $M : XO_4 = 1 : 2$.

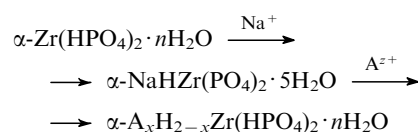
Initial state	H^+		Li^+		Na^+		K^+		Ref.
	n	$d, \text{\AA}$	n	$d, \text{\AA}$	n	$d, \text{\AA}$	n	$d, \text{\AA}$	
100% substitution									
$\alpha\text{-Ti}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$	1	7.60	1	7.6	3	9.9	3	10.4	33
$\alpha\text{-Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$	1	7.56	1	8.50	3	9.88	3	10.70	208, 220
$\gamma\text{-Ti}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$	2	11.62	2	11.3	2	12.8	3	14.2	33
$\text{H}_5\text{O}_2\text{Ta}(\text{PO}_4)_2$	2	9.50	2	9.08	3	10.96	1	8.89	39
50% substitution									
$\alpha\text{-Ti}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$	1	7.60	1	7.6	4	10.4	—	—	33
$\alpha\text{-Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$	1	7.56	3	10.1	5	11.87	—	—	222
$\gamma\text{-Ti}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$	2	11.62	1.5	11.3	3	13.2	0	10.8	33

**Figure 9.** Dependence of the interlayer distance in the acid phosphates of tetravalent elements on the degree of hydration (a) and on the radius of the alkali metal cation in $\text{AHB}(\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$ (b). (a) (based on the data of Llavona *et al.*³³ and Poojary and Clearfield²²⁰): (1) $\gamma\text{-NaHTiP}$; (2) $\alpha\text{-NaHZrP}$; (b) (based on the data of Llavona *et al.*³³ and Scou *et al.*²²²): (1) $\gamma\text{-MHTiP}$; (2) MTaP .

first cation, the $[\text{M}(\text{XO}_4)_2]_n$ layers move apart and the insertion of a second cation between them becomes preferred to the migration of the singly substituted phase front into the bulk of the specimen. In particular, this conclusion has been confirmed by the possibility of obtaining $\alpha\text{-KHZr}(\text{PO}_4)_2$ by other methods.²¹⁹ The removal of this limitation and the weakening of the interaction forces between the layers, for example for $\gamma\text{-Zr}(\text{HPO}_4)_2$, leads to the formation of two intermediate phases with degrees of substitution of 25% and 50%, in the course of the exchange.³³ In the case of tantalum hydrogenphosphate with an even weaker interaction between the layers, the solid solutions $\text{M}_x\text{H}_{1-x}\text{Ta}(\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$ are formed.³⁹

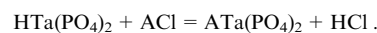
The proton/alkali metal cation ion-exchange processes in acid phosphates of polyvalent elements are due to the high mobility of the hydrogen ions and the incoming cations, which increases with increase in the degree of hydration and diminishes with increase in the radius and content of the alkali metal.^{39, 224} The attempt to

achieve the exchange of the protons of acid tin phosphate for Cu^{2+} cations showed that the ion exchange occurs only on the surface.²²⁴ This is caused by the fact that the diffusion of doubly charged cations is kinetically hindered and that the double tin copper phosphate with a low mobility of the cations is formed on the surface. The nuclei of the new phase produced cover the conductivity channels and prevent further exchange.²²⁴ However, it was possible to obtain the product $\text{MgZr}(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ by refluxing titanium hydrogenphosphate with magnesium acetate.²²⁵ This method makes it possible to increase the diffusion coefficient by carrying out the process at an elevated temperature and by working in the region of comparatively low pH values, which are determined by the ratio of the concentrations of acetate ions and acetic acid in solution. An alternative method of synthesis of compounds with doubly and triply charged cations involves their preparation from the sodium-form of zirconium α -phosphate in accordance with the mechanism proposed by Scou *et al.*²²⁶



Magnesium zirconium hydrogenphosphate $\alpha\text{-Mg}_{0.5}\text{HZr}(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ and chromium zirconium hydrogenphosphate $\alpha\text{-Cr}_{0.5}\text{H}_{0.5}\text{Zr}(\text{HPO}_4)_2 \cdot 5\text{H}_2\text{O}$ were thus synthesised at room temperature. The sorption of the ions $[\text{Ru}(\text{NH}_3)_6]^{2+}$ from the corresponding aqueous solution has been achieved similarly (with the intermediate formation of the ammonium analogue).²²⁷

The hydrated acid phosphates can be obtained from the potassium salts $\text{K}_x\text{Sb}_x\text{P}_{2-x}\text{O}_{3x+5}$ by ion exchange with inorganic acids at an elevated temperature,²²⁸ but this process is slow. The substitution of potassium in $\text{KTa}(\text{PO}_4)_2$ takes place more simply.²¹¹ Chernorukov *et al.*²²³ obtained double tantalum alkali metal phosphates by solid-phase synthesis from finely disperse tantalum hydrogenphosphate and the corresponding chlorides and hydroxides at 200–400 °C.



The corresponding process cannot be carried out in solution owing to the hydrolysis of the tantalum hydrogenphosphate. However, the synthesis of the coarsely crystalline compound using the method proposed by Yaroslavtsev and Nikolaev²¹¹ made it possible to achieve proton/alkali metal cation ion-exchange in aqueous solutions.^{17, 39}

A multiplicity of other materials with ion-exchange and catalytic properties as well as proton conductivity have been obtained from hydrogenphosphates of polyvalent elements. Among them, mention should be made of a mixed zirconium hydrogenphosphate-arsenate²¹⁹ and numerous phosphonates and mixed phosphate-phosphites, which have been extensively investigated in recent years as promising ion exchangers with a high selectivity.^{31, 230–235} The products of the intercalation of amines, alcohols, and other organic derivatives, containing functional groups and capable of forming bonds with a proton in the structure of acid zirconium phosphate, have also been studied intensely.^{44, 236–245}

b. Structures of the NASICON type

Hydrogenphosphates of tetravalent elements with the ratio $\text{M}^{\text{IV}} : \text{XO}_4 = 2 : 3$ belong to the NASICON structural type. They have become widely known by virtue of the high cationic conductivity⁸ of a series of solid solutions $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$.^{246, 247} A series of compounds $\text{A}^{\text{I}}\text{B}_2^{\text{IV}}(\text{PO}_4)_3$, where A^{I} is an alkali metal cation, while B^{IV} is the cation of a tetravalent metal, which is usually zirconium, have been synthesised. Solid-

§ Their name 'Na super-ion conductor' (NASICON) is due precisely to this property.

phase or hydrothermal synthesis as well as synthesis from the melt are normally employed.^{248–255}

The joining together of BO_6 octahedra and PO_4 tetrahedra is characteristic of the NASICON type crystal structure, but, in contrast to the layered phosphates examined above, all the oxygen atoms of the anion participate in the formation of the $\text{P}–\text{O}–\text{B}$ linkages. Channels extending along the crystallographic c axis are formed in the three-dimensional lattice. However, whereas 75% of the cavities remain unoccupied in $\text{NaZr}_2(\text{PO}_4)_3$,^{247, 249} they are all occupied in $\text{Na}_4\text{Zr}_2(\text{SiO}_4)_3$.^{256, 257} All the oxygen atoms in the structure described are simultaneously coordinated to quadruply and quintuply charged cations and they therefore possess comparatively weak electron-donating properties. Together with the partial occupation of the cavities, this ensures a high mobility of the cation and the possibility of the occurrence of ion-exchange reactions.

The cation exchange in the compounds $\text{A}^{\text{I}}\text{B}_2^{\text{IV}}(\text{PO}_4)_3$ is most often carried out by treating the initial phase with salt melts. The lithium, potassium, and silver derivatives can be obtained in this way from the sodium phase.^{8, 258–260} The attempts to obtain the hydrogen-form of zirconium phosphate by treating the sodium or ammonium compound with an acid under hydrothermal conditions were unsuccessful.²⁵⁴ $(\text{H}_3\text{O})\text{B}_2^{\text{IV}}(\text{PO}_4)_3$ was obtained by the interaction of $\text{LiZr}_2(\text{PO}_4)_3$ or $\text{LiTi}_2(\text{PO}_4)_3$ with an acid⁷ and also as a result of the heat treatment of $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ with subsequent maintenance of $\text{HZr}_2(\text{PO}_4)_3$ in water.²⁶¹ The substance obtained can serve in its turn as the initial basis for the synthesis of derivatives with other monovalent ions. Thus the preparation of $\text{LiTi}_x\text{Zr}_{2-x}(\text{PO}_4)_3$ by ion exchange with lithium hydroxide under hydrothermal conditions has been described.²⁶²

In contrast to layered phosphates, the three-dimensional lattice of compounds with a NASICON type structure changes little when the cations are varied. However, there are structures of this type differing in symmetry. The assignment of a substance to a particular structural type is determined primarily by the number of singly charged cations per formula unit. The compounds $\text{A}_3\text{B}_2^{\text{III}}(\text{PO}_4)_3$, where $\text{B}^{\text{III}} = \text{Sc}, \text{B}, \text{or Fe}$,^{263–266} exhibiting ion-exchange properties and cationic conductivity, have been obtained. As in the $\text{NaZr}_2(\text{PO}_4)_3$ structure, the number of singly charged cations (A^{I}) is found to be smaller than the number of sites available for their accommodation. Sodium and lithium ions are then found to be statistically distributed between a pair of possible sites with nonequivalent populations, forming the so called statistical dipoles.^{263, 264, 267}

c. Compounds based on the structure of NbOPO_4 and its derivatives

The oxide phosphates BOXO_4 (where B is, for example, V, Nb, or Mo and X = P or As) are characterised by one of the simplest types of isostructure, formed by the joining together of BO_6 octahedra and XO_4 tetrahedra. The crystal lattice of the oxyphosphates of pentavalent vanadium, niobium, and molybdenum is made up of planes of tetrahedra of phosphate anions and metal octahedra joined together by four vertices (Fig. 10a).

The two remaining vertices of the octahedron are in the *trans*-position relative to one another and are combined with the analogous vertices of adjacent layers, ensuring bonding between them as a result of the formation of the $–\text{O}–\text{B}–\text{O}–\text{B}–\text{O}–$ bridges.^{268–270} The BOXO_4 structures are distinguished by a significant nonequivalence of the metal–oxygen bonds: one of the bonds formed is close to being a double bond, whilst the other is close to a very weak coordinate bond (Table 7).

By virtue of the features listed above, the intercalation of water molecules in compounds of this kind is possible.^{278–281} This process proceeds particularly readily in vanadium oxyphosphate, the cation of which tends to form multiple bonds. Here it is assumed that, on dissociation of the $–\text{O}–\text{V}–\text{O}–$ chain of bonds, $\text{H}_2\text{O}–\text{V}=\text{O}$ fragments are formed and the planes $(\text{H}_2\text{VO}_2\text{PO}_4)_n$ move apart in space, forming a layered structure (Fig. 10b).^{271, 272} The positions of protons and of the second water molecule in $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ have not been determined. The formation of

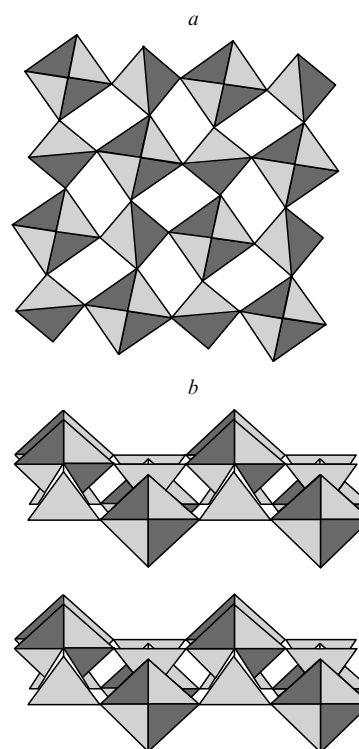


Figure 10. Fragments of the VOPO_4 (a) and $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ (b) structures.

Table 7. The metal–oxygen bond lengths in certain compounds based on the NbOPO_4 structure.

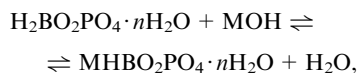
Compound	The length of B–O bonds in octahedron /Å			Ref.
	B–O–(X)	B–O–(B)	B=O	
NbOPO_4	1.97	1.78	2.32	269
MoOPO_4	1.97	1.66	2.63	268
VOPO_4	1.87	1.58	2.87	270
$\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$	1.92	1.43	2.49	271, 272
$\text{NH}_4(\text{VO}_2)(\text{HPO}_4)$	1.92	1.57	1.69	273
$\text{HUO}_2\text{PO}_4 \cdot 4\text{H}_2\text{O}$	2.31	1.75	1.78	274
KMnO_2PO_4	1.98, 2.19	1.69	1.69	275
KTiOPO_4	1.99	1.72	1.98	276, 277

compounds with a higher degree of hydration is also possible. Analogous transformations under the influence of a hydrochloric acid solution occur in niobium oxide phosphate, where the metal–oxygen bonds differ less.²⁸¹ It has been established by NMR that the monohydrate and trihydrate contain two hydroxy groups, not bound to the phosphorus, per cation, (*i.e.* these substances are niobium hydroxophosphates $\text{Nb}(\text{OH}_2)\text{PO}_4$ and $\text{Nb}(\text{OH})_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$).²⁸¹

The compounds formed may split off protons, which can migrate in the interlayer space. This follows, in particular, from the evident analogy between the structure of the hydrated oxyphosphates and uranyl phosphate — one of the best proton conductors at room temperature ($1.8 \times 10^{-3} \text{ S cm}^{-1}$).^{274, 282} The conductivity of niobium oxyphosphate trihydrate is lower almost by an order of magnitude ($3 \times 10^{-4} \text{ S cm}^{-1}$), probably as a consequence of the less-developed system of hydrogen bonds, while the activation energies for this process are virtually identical in the two compounds.²⁸¹ The conditions in the interlayer space are favourable for the migration of cations. Thus, conditions for ion-exchange processes are created in a series of compounds

$\text{BOX}_4 \cdot n\text{H}_2\text{O}$, $\text{H}_3\text{OMoO}_2\text{PO}_4$ and its potassium analogues have similar structures, although the metal–oxygen bonds are then in the *cis*-position in the molybdenum coordination polyhedron.^{275, 283}

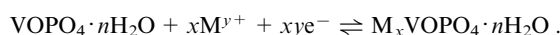
Hydrated vanadium and niobium oxyphosphates exhibit ion-exchange properties on interaction with solutions of alkalis, substituting one of the protons by a cation *via* the reaction^{284–287}



where $\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$, or NH_4 .^{284–287} The lengths of the metal–oxygen bonds are then significantly equalised even in the vanadium derivatives $\text{NH}_4(\text{VO}_2)(\text{HPO}_4)$ ²⁷³ and there is a simultaneous rearrangement of the structure with migration of the proton to the anion and the formation of a vanadium coordination polyhedron in the form of a square pyramid.²⁸⁸ The compound $\text{LiHBO}_2\text{PO}_4$ with a high lithium conductivity has been obtained by the heat treatment (500 °C) of the products of the interaction of niobium oxyphosphate with lithium hydroxide.²⁸⁷

In uranyl phosphate, the oxygen atoms of the anion are coordinated to the metal and the remaining two participate in the formation of the uranyl ion. The ‘anionic part of the framework’ therefore manifests weak proton-accepting properties and the proton is transferred to the proton hydrate sub-lattice $\text{H}^+ \cdot 4\text{H}_2\text{O}$ localised in the interlayer space.²⁷⁴ This is responsible for the high ionic conductivity and the distinct ion-exchange properties. Oxonium ions are readily substituted by an alkali or alkaline earth metal ion.²⁸⁹ Uranyl phosphate readily sorbs cations even from dilute aqueous systems with formation of solid solutions. All the compounds formed have a fairly high ionic conductivity.^{192, 291–293}

Another type of ion-exchange processes, occurring in hydrated vanadium oxyphosphate, is the reductive intercalation of hydrogen and singly or doubly charged cations with partial reduction of vanadium *via* the reaction^{278, 293–298}



An intermediate degree of oxidation of vanadium in the range $4 < z < 5$ was most frequently attained, but in the case of the reductive intercalation of lithium and hydrogen the limiting case with $x = 1$ occurred. The compounds $\text{AVOPO}_4 \cdot n\text{H}_2\text{O}$ can then be considered as the reduction products.²⁹⁸ These substances may give rise to several crystal structures, differing in the type of binding of the octahedra and in the number of molecules of the water of hydration. A characteristic feature of these substances is the presence of the vanadyl ion with a shortened metal–oxygen distance (~ 1.5 Å). Three sites in the equatorial plane are occupied by the oxygen atoms of the anion and one site is occupied by the oxygen of water or the vanadyl ion ($R_{\text{V}-\text{O}} \approx 2.0$ Å). Weakly coordinated water molecules or the oxygen of a neighbouring vanadyl cation ($R_{\text{V}-\text{O}} \approx 2.3$ Å) are located in the *trans*-position relative to the oxygen of the $\text{V}=\text{O}$ group.^{298–301}

In compounds of the type $\text{VOHPO}_4 \cdot n\text{H}_2\text{O}$ the hydrogen phosphate anions are highly polarised and may dissociate with elimination of the proton. The substance formed on substitution of such a proton by an alkali metal cation retains the ability to exchange the latter for other cations (Na^+ , K^+ , Rb^+ , NH_4^+ , Ag^+ , Ti^+).^{303–306} The substitution products AVOPO_4 are constructed from distorted VO_6 octahedra, combined into chains *via* a pair of common vertices, and from PO_4 tetrahedra bound to them.³⁰⁶ Such compounds belong to the KTiOPO_4 structural type characterised by the presence of channels along the crystallographic *c* axis,^{276, 277} which are responsible for the ionic mobility and the ion-exchange properties.²⁶⁵

V. Conclusion

The data presented in the review show that inorganic sorbents are promising materials for the separation and extensive purification

of various ions, including alkali metal cations, which are difficult to separate by other methods. Such ion exchangers are characterised by a high radiation stability and by the ability to sorb heavy metal cations. They are therefore actively employed in the atomic industry. The ability to extract selectively a series of cations from a large number of competing ions of the main substance is quite important. Inorganic sorbents are widely employed for the creation of different kinds of materials with an extensive specific surface, catalytic properties, and ionic conductivity. Furthermore, with the aid of ion exchange it is possible to obtain a series of substances, the synthesis of which by other methods is impossible owing to the thermodynamic instability of the initial compounds or the kinetic inhibition of their reactions.⁸¹ All this provides grounds for the hypothesis that the use of inorganic sorbents will expand.

We believe that the employment of ion-exchange processes as model reactions for the comprehensive study of the thermodynamic and kinetic characteristics of certain phenomena occurring in solids (for example, the diffusion of ions, solid-phase reactions, *etc.*) is also promising. The possibility of selecting substances with different sizes of cavities, conductivity channels, and interplanar spacings makes it possible to trace in detail the influence of these parameters on the dynamics of the processes considered and to investigate the dependence of the affinity of the structure for particular ions on the geometry and nature of their potential environment, rigidly specified by the structure of the ion-exchange matrix. The simplicity and high accuracy whereby the changes in the concentrations of the reactants in solution may be monitored permit the modelling of many processes in solids.

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Oxo-acidity in ionic melts

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Abstract. The current state of research into the oxo-acidity in alkali metal nitrate, sulfate, and halide melts is analysed on the basis of the proposed classification of oxo-acidity reactions (Lux–Flood acid–base interactions). It is established that a considerable proportion of literature data on homogeneous acid–base equilibria are incorrect, since no account is taken in them of either the levelling of the acid (basic) properties by the solvent or of the error in the determination of the reaction stoichiometries. An explanation is proposed for the considerable scatter of data on the solubilities of oxides in ionic melts, which has been the principal inhibiting factor in the development of this field. The reactions of melts with gaseous acid and basic reagents are examined. The bibliography includes 171 references.

I. Introduction

Ionic melts are widely used in science and engineering as media for various processes such as electrolysis, electrochemical synthesis, the growing of single crystals, *etc.* The virtually complete dissociation of the solvents into constituent ions makes it possible to generate high current densities in electrolysis. In the absence of oxidants, for example H^+ , it is possible to obtain in ionic melts products which cannot be isolated from aqueous solutions (alkali and alkaline earth metals, subions, *etc.*). From the standpoint of the protection of the environment, the application of fused salts as technological solvents is specially attractive, because their use does not entail the accumulation of liquid industrial waste.

The processes in solvent melts are appreciably influenced by the impurities present in the initial salt starting material or formed during the fusion of the solvents as a consequence of high-temperature hydrolysis or the interaction of the melt with the material of the container and the corrosive components of the atmosphere. Such impurities include impurity metal cations and various oxygen-containing anions (sulfates, carbonates, hydroxides). The strength of the effect of the anions on the processes in ionic melts depends mainly on the degree of their dissociation with formation of the oxide ion O^{2-} as one of the products.

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Reactions involving the transfer of oxide ions in ionic melts are usually regarded as acid–base interactions (oxo-acidity); their treatment is then based on the ideas proposed by Lux¹ and developed in the studies of Flood and coworkers:^{2–4}



where A is an acid and B a base. The oxygen index pO, analogous to pOH in aqueous solutions, serves as a quantitative measure of the basicity (acidity) of fused media:

$$pO \equiv -\lg a_{O^{2-}} \sim -\lg m_{O^{2-}},$$

where $a_{O^{2-}}$ and $m_{O^{2-}}$ are the activity and molality of the oxide ions in the melt respectively.

Although studies on oxo-acidity have been carried out since 1939,¹ hitherto no attempt has been made to survey or treat systematically the results obtained and the available information about oxo-acidity in ionic melts consists of a set of scattered and frequently incorrect data. The present review is intended to fill the existing gap. It is possible to identify the following main trends in studies on oxo-acidity in ionic melts:

- homogeneous (intrinsic acid–base) reactions;
- dissolution and dissociation of oxides in melts;
- interaction of melts with gaseous reagents, including high-temperature hydrolysis of the melts, elimination of oxygen-containing impurities, and dissociation of Lux–Flood bases (CO_3^{2-} , OH^- , *etc.*).

II. Homogeneous acid–base equilibria

1. Specific features of ionic melts as media for acid–base interactions

Ionic melts as media in which Lux–Flood acid–base interactions take place may be divided into two classes depending on the presence in them of constitutional oxygen ions (*i.e.* ions entering into the composition of the main components of the melts): oxygen-free and oxygen-containing. We shall consider the characteristic features of the acid–base interactions in melts of the types indicated.⁵

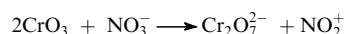
Oxygen-free melts do not contain constitutional oxygen and the ‘pure’ melt cannot therefore serve as a O^{2-} donor. However, as a consequence of the inevitable contamination of the melt by oxygen-containing impurities such as SO_4^{2-} , CO_3^{2-} , and OH^- , in practice oxygen-free melts nevertheless always contain a certain amount of oxide ions. The concentration of oxide ions in the ‘pure’ solvent melt is not constant but depends on the content of impurities and the degree of their dissociation with formation of O^{2-} , which increases in the sequence $SO_4^{2-} < CO_3^{2-} < OH^-$.

In the 'pure' oxygen-free melts, the pO is usually in the range 3–4.5. The use of even the strongest halogenating agents does not permit a significant decrease in the O^{2-} concentration and this is the 'inevitable fault' leading to errors in potentiometric measurements especially when small amounts of the test substances are added. However, in a number of instances the pO of the 'pure' halide melt is used as the 'internal standard' of the melts for the construction of acidity scales.^{6–9}

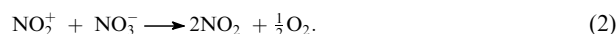
In oxygen-containing melts, the acid–base reactions are more complex, since in this case a competing equilibrium acid–base autodissociation of the solvent-melt takes place. A characteristic feature of the oxygen-containing melts is the presence in the latter of not only the base but also of the solvent-acid. This renders oxygen-containing melts similar to low-temperature solvents with an intrinsic acid–base equilibrium.¹⁰

However, oxygen-containing melts also possess a series of characteristic features due to the relatively high temperature of the liquid state. Very often, the solvent-acid is volatile or unstable^{1,11} and is gradually removed from the acid melt as a consequence of decomposition or evaporation, while the pO in such a solution gradually approaches the corresponding value for a neutral melt. For this reason, very frequently not only are the acid properties levelled off in oxygen-containing melts but an upper acidity limit is also established.

Thus it has been observed that the highest chromium and molybdenum oxides decompose a nitrate melt with evolution of NO_2 and with increase in temperature the e.m.f. of a cell with an oxygen electrode is appreciably reduced.¹² It has been suggested that the nitrogen(V) oxide and the corresponding anions are formed in the interaction of the oxides with the melt. Since the acids indicated are very strong, one may postulate that the process



is fully displaced to the right and that the acid strength is determined by the acid properties of the nitronium cation NO_2^+ . The stability of the latter is low and, after the attainment of certain concentration, its reaction with the melt anions becomes fairly intense:

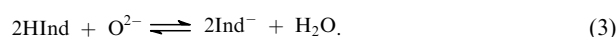


The kinetic methods for the determination of the acidity of the melt are based on this reaction. As reaction (2) occurs, the concentration of the nitronium cation diminishes and the rate of the process falls. Ultimately it becomes so low that a constant e.m.f. is observed in a series of consecutive measurements. This is in fact the upper acidity limit in the melt, which is independent of the type of acid. The above considerations make it possible to explain readily the temperature dependence observed by Shams El Din and El Hosary:¹² an increase in temperature leads not only to a decrease in the stability of the nitronium cation but also to an increase in the rate of process (2).

The presence of an upper acidity limit is also characteristic of sulfate melts, which is apparently associated with the limited solubility of SO_3 in the latter. This is indicated by the drift of the e.m.f. (pO) in the acid-containing melt towards the neutral point.¹

2. Methods of investigation

Most diverse methods are used to investigate oxo-acidity and to estimate the acid properties of melts. The simplest is the indicator method, the essential feature of which has been described by Brough *et al.*¹³ The behaviour of 11 acid–base indicators used in aqueous solutions has been investigated in the melts KNO_3 – $LiNO_3$ at 210 °C and KSCN at 200 °C. The colour transitions of the indicators (Ind), associated with the change in the acidity of the medium on titration of an alkali or sodium peroxide with potassium pyrosulfate were examined:



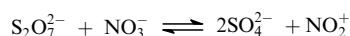
In the nitrate melt, only the colour of phenolphthalein changed (yellow → purple), whilst the remaining indicators were apparently oxidised. In the KSCN melt, which has no oxidative properties, colour transitions were observed for all the indicators investigated (Methyl Red, thymolphthalein, *etc.*).

The use of indicators for the investigation of acidity is limited primarily by their thermal instability and by their ready oxidisability at high temperatures. Since ionic melts do not as a rule contain water, the transition of the indicator to the protonated form [reaction (3)] is hardly possible (the yellowing of the solution in the reverse transition of phenolphthalein has been noted¹³). The indicator method can therefore be used only in the study of relatively low-temperature melts (< 250 °C).

The application of spectroscopic methods for the study of the basicity of melts has been described.^{14,15} Duffy *et al.*¹⁴ constructed an 'optical' basicity scale for metallurgical slags relative to CaO adopted as the standard. The optical basicity was determined by estimating the changes in the frequencies of the spectral lines (the $^1S_0 \rightarrow ^3P_1$ transition) of the Tl^+ , Pb^{2+} , and Bi^{3+} cations in a basic medium. X-Ray fluorescent spectroscopic study of the Na_2O – B_2O_3 – Al_2O_3 , Na_2O – B_2O_3 – SiO_2 , and Na_2O – SiO_2 – Al_2O_3 melts showed that the relative acidity of the oxides diminishes in the sequence $B_2O_3 > SiO_2 > Al_2O_3$.¹⁵ The spectroscopic methods require as a rule the use of cooled (quenched) specimens, which may affect the validity of the results obtained in view of the discrepancy between the temperature of the melt investigated and the temperature at which the acid (basic) properties are estimated.

There are data obtained in the study of the basicity of melts by measuring the solubility in the latter of acid gases.^{16,17} The solubility of sulfur(VI) oxide in sodium phosphates has been determined by a gravimetric method and a correlation has been established between the basicity of the melt and the solubility of the acid gas in the latter.¹⁶ Iwamoto¹⁷ used CO_2 and H_2O in order to determine the basicity. However, such methods are applicable only to basic melts, because the acids present in stable acid melts displace the indicator acid gas. Furthermore, the products of the interaction of the acid gas with basic melts are stable, which leads to an irreversible change in the properties of the latter.

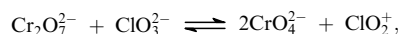
The so called 'kinetic' method has been proposed for the estimation of the acidity of alkali metal nitrate melts. The interaction of nitrate melts with pyrosulfate ions^{18,19}



leads to the formation of the nitronium cation, which subsequently interacts with nitrate ions in accordance with Eqn (2). The latter reaction is the slowest and the overall acidity of the medium can be inferred from its rate:

$$T_A = [S_2O_7^{2-}] + [NO_2^+].$$

The interaction of dichromate ions with chlorate ions in the KNO_3 – $NaNO_3$ melt involves the occurrence of two reactions:^{20,21}

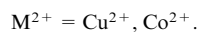
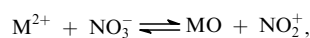


Reaction (4) is rate-limiting. The rate of evolution of chlorine is proportional to the quantity

$$T_A = [Cr_2O_7^{2-}] + [ClO_2^+].$$

The interaction of bromate ions with dichromate in a nitrate melt has been studied.²² The cations investigated can be arranged in the sequence $BrO_2^+ < ClO_2^+ < NO_2^+$ in terms of their acidity. We suggest that the introduction of the overall quantity T_A by the above investigators^{18–24} unjustifiably complicates the analysis of the results, because the acidity of nitrate melts is determined solely by the concentration (activity) of NO_2^+ ions and the rates of the rate-limiting reactions (2) and (4) depend only on the concentrations of the cations NO_2^+ and ClO_2^+ respectively.

The kinetic method has been used also to investigate the acidity of the Cu^{2+} and Co^{2+} cations in the $\text{KNO}_3\text{--NaNO}_3$ melt at temperatures in the range 325–375 °C.^{23,24} The acidity was determined from the rate of reaction (2). The nitronium cation was formed in solution *via* the reaction



The acidity of the cations of these metals was found to be close to that of the dichromate ion and the cations investigated by Duke and coworkers.^{18–22} Evidently Slama^{23,24} made a definite error in the estimation of the acidity of the cations, because the degree of binding of the oxide ions O^{2-} by the latter is determined not only by their active properties but also by the formation of a new phase — the corresponding oxides, which are virtually insoluble in the test melt.

The deficiencies of the methods described prevent their wide-scale employment for the investigation of the oxo-acidity of metals over a wide temperature range.

The method based on the e.m.f. of cells with transport in which an oxygen indicator electrode, reversible with respect to O^{2-} ions, is employed is the most promising. The electrochemical cells can be represented as follows in a general form:

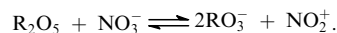


In the familiar potentiometric studies, it has been postulated that the diffusion potential is zero. Either a metallic electrode (*i.e.* a metal immersed in a solution of the salt of the corresponding cation at a definite concentration) or an oxygen electrode immersed in a solution with a known or constant concentration of oxide ions (concentration cells) have been used as reference electrodes.

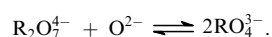
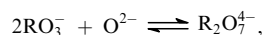
3. Nitrate melts

Since a large number of publications have been devoted to studies of the oxo-acidity of nitrate melts, these systems are traditionally regarded as most thoroughly investigated. The relatively low melting points of both individual alkali metal nitrates and of their mixtures permit the employment of comparatively simple experimental apparatus. Potentiometric studies in nitrate melts reduce mainly to the determination of the acid–base equilibrium constants.

The greatest number of publications concern the studies of the oxo-acidity of the KNO_3 melt at 350 °C.^{12,25–49} The results of the determination of the constants for the addition of the oxide ion to higher oxides and anions of Group V elements (P, As, V) have been published.^{25–30} All the oxides investigated react with the nitrate melt to form the salts of the corresponding meta-acids:



Reaction (2) displaces the equilibrium to the right. Nitrogen(IV) oxide is evolved until the e.m.f. decreases to ~ 0.5 V, which, judging from the results of other studies, corresponds to the upper limit of acidity in the KNO_3 melt.^{25–30} According to these data,^{25–30} the acid–base product for the solvent is $\sim 10^{-16}$. As the titrant Na_2O_2 is added, the following reactions take place consecutively in the melt:

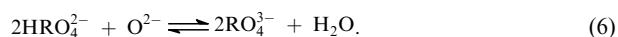


$\text{R} = \text{P, As, V}.$

The acid properties of the oxide intensify in the sequence $\text{V}_2\text{O}_5 < \text{P}_2\text{O}_5 < \text{As}_2\text{O}_5$.

Apart from these reactions, the equilibria which according to Shams El Din *et al.*^{25–27} are established when the ions HPO_4^{2-} , H_2PO_4^- , HAsO_4^{2-} , and H_2AsO_4^- , added to the melt are titrated

have also been investigated. The equilibrium constants of the reactions

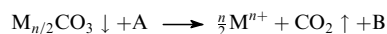


were determined. However, even pure salts, incorporating the corresponding anions, decompose at temperatures very appreciably below 350 °C, forming the corresponding meta- and pyro-salts.⁵⁰ In the absence of water vapour, equilibria (5) and (6) cannot therefore occur.

The study of the acid properties of the highest oxides of Group VIB,^{12,31,32} showed that chromium(VI) and molybdenum(VI) oxides react with the nitrate melt, forming the dichromate and trimolybdate ions respectively. After the cessation of the evolution of NO_2 , the e.m.f. is close to 0.5 V, which agrees with the values obtained for the oxides of Group V elements.^{25–30} The products of the interaction of chromium and molybdenum oxides with the melt are titrated in one stage and the final products of the neutralisation reactions are the chromate and the molybdate respectively. Tungsten(VI) oxide is a weaker acid and does not decompose the pure melt. Its titration takes place in one stage and the product is tungstate ions. The acidity of the oxides investigated increases in the sequence $\text{WO}_3 < \text{MoO}_3 < \text{CrO}_3$.

The published equilibrium constants K ^{12,25–40} cannot be called correct because the calculated values vary during titration within the limits of several orders of magnitude of $\text{p}K$. This occurs either owing to the incorrect selection of the participants in the equilibrium (the stoichiometry) or because the authors did not calibrate in an ‘acid’ medium the oxygen electrode $\text{Pt}(\text{O}_2)$ employed.

It has been established by the method involving the titration of the corresponding carbonates by dichromate³⁴ and metaphosphate³⁵ ions, *i.e.*



that the acidity of the cations increases in the sequence $\text{K}^+ < \text{Na}^+ < \text{Li}^+$, $\text{Ba}^{2+} < \text{Sr}^{2+} < \text{Ca}^{2+} < \text{Pb}^{2+}$. Although this sequence agrees satisfactorily with the electronegativity series of the metals, nevertheless this method for the examination of acidity must be regarded as unsuccessful because the acids employed by the investigators for the titration not only eliminate oxide ions from the carbonates but can also form insoluble chromates and phosphates with the majority of the cations. The formation of complexes or precipitates is demonstrated by the position of barium in this series, the acidity of which is comparable to the acidity of potassium and sodium and is appreciably lower than the acidity of lithium. This might have influenced also the positions of a number of other alkaline earth metals in the series considered.

The relative Lux–Flood base strengths in nitrate melts have been investigated.^{36,37} The bases investigated were separated into two groups: the oxide ions (OH^- , O^{2-} , and O_2^{2-}) and the carbonate ions [CO_3^{2-} , HCO_3^- , $(\text{COO})_2^{2-}$, CH_3COO^- , HCOO^-]. The first group includes the bases, which, according to the authors, dissociate fully in the melt with formation of oxide ions. The second group is made up of weak bases. Since they all decompose at the experimental temperature (350 °C) with formation of the carbonate ion, the differences between separate representatives of this group are confined to their reducing properties: by reducing nitrate ions, organic acid salts promote the accumulation in the melt of excess amounts of oxide and carbonate ions compared with the stoichiometric concentrations. The majority of the bases investigated are therefore unsuitable for quantitative studies.

There exists the view³⁷ that oxide ions are present in nitrate melts in the form of pyronitrate ions, which are strong bases with strengths comparable to that of carbonate ions. From the contemporary point of view, the existence of the pyronitrate ion is doubtful, because the coordination number of nitrogen with respect to oxygen cannot exceed 3, whilst in the hypothetical

pyronitrate it is 4. It has been shown³³ that the pyronitrate ion is not formed in basic melts. Oxide ions can be stabilised in the melt solely by virtue of the formation of silicate ions in the reaction with the material of the container (Pyrex).

The communications of Shams El Din and Gerges^{39,40} also contain data on the behaviour of oxygen electrodes in nitrate melts. The 'anomalous' behaviour of the platinum oxygen electrode has been attributed to the 'peroxide' function of oxygen gas electrodes. On the other hand, a satisfactory reversibility is characteristic of metal oxide electrodes (of the second kind).

Experimental study of the acid–base equilibria involving phosphates and molybdates led to the conclusion that heteropolyacids are formed in nitrate melts.^{41,42} This has been confirmed by the results of cryoscopic studies.⁴³ Certain characteristic features of the potentiometric titration method in melts have been described.^{44,45} The automatic titration method consists of the following features:⁴⁴ a rod of the solidified solution of $K_2Cr_2O_7$ in the test melt is lowered at a uniform rate, by means of a special device, into the melt containing the base and the pen recorder measures the e.m.f.'s. This method makes it possible to estimate only the concentration of the acid in the test melt (to within 3.5% according to the authors). The thermodynamic characteristics could not be determined because the measured e.m.f. does not correspond to equilibrium.

With increase in the acidity of the oxide, the decomposition temperature of the nitrate melt falls.⁴⁶ This has been explained by the decrease in the activation energy for the decomposition reaction as a result of the binding of the oxide ions formed by acids. However, the observed phenomenon can be explained also, without resorting to kinetic ideas, by the shift of the decomposition equilibrium towards the formation of oxide ions and nitrogen oxides in accordance with the Le Chatelier rule. The affinity of the oxide decreases in the sequence $SiO_2 > TiO_2 > ZrO_2 > Al_2O_3 > MgO$.

A study of the possibility of using a series of metal oxide oxygen electrodes ($Nb|Nb_2O_5$, $Ta|Ta_2O_5$, $Zr|ZrO_2$) in potentiometric studies^{47–49} made it possible to construct the following acidity series in the potassium nitrate melt at 350 °C: $NH_4VO_3 > NaPO_3 > NaH_2PO_4 > K_2Cr_2O_7 > K_2HPO_4 > Na_4P_2O_7 > NaH_2AsO_4 > K_2CO_3 > Na_2O_2$.

The presence in this series of certain acids, the existence of which is doubtful, shows that the authors did not always take into account the real processes occurring in the melt. Thus it is quite clear that ammonium metavanadate should decompose to the oxide V_2O_5 , which is partly reduced by ammonia, whilst acid salts decompose to the corresponding pyro- and meta-salts. The above acidity series cannot therefore be regarded as uncontroversial.

4. Sulfate melts

The intrinsic acid–base dissociation equilibrium is established in sulfate melts:



Such systems have been investigated to a much smaller extent than the nitrate melts, which can be explained by the relatively high melting points of both the individual sulfates and their eutectic mixtures. Another possible cause is the very low stability of the acid solutions in such melts. Indeed, reaction (7) should lead to the formation in the melt of SO_3 , which is a gas at the melting points of the known eutectic mixtures of alkali metal sulfates. The sulfate melts may contain SO_3 as a result of the formation of polysulfates, for example the pyrosulfate $SO_3 \cdot SO_4^{2-}$. According to reference data,^{50,51} the decomposition temperatures of pure pyrosulfates do not exceed 460 °C and in solution they should be even lower. Under the conditions of continuous renewal of the atmosphere over the melt, *i.e.* in an argon or nitrogen stream, the process involving the evaporation of the acid SO_3 from the sulfate melt, *i.e.*



should be displaced fully to the right according to the Le Chatelier rule and equilibrium cannot be attained in acid solutions. From the standpoint of the study of oxo-acidity, the eutectic mixture of potassium, lithium, and sodium sulfates (0.135 : 0.78 : 0.085) with a melting point of 512 °C may prove to be the most promising.⁵² In this case, studies may be carried out at lower temperatures than in the classical study¹ and hence acid and basic solutions will be more stable.

The oxygen electrode $Pt(O_2)$ has been calibrated and an acidity scale has been constructed¹ in the K_2SO_4 – Na_2SO_4 melt at 800 °C. The study of the thermal stability of the pyrosulfate showed that the enhancement of the acidity of the cations of the melt lowers the decomposition temperature of the latter.³

Measurements of the acidity of centimolar solutions of sodium pyrosulfate and peroxide showed that the extent of the acidity scale in the K_2SO_4 – Li_2SO_4 – Na_2SO_4 melt at 550 °C amounts to 10 pO units.^{53,54} Hence it is easy to determine the acid–base product for the solvent: it is 10^{-14} . The range of stability of the VO^{2+} ion is $pO = 8.5$ – 10.6 .

In conclusion of the topic of oxo-acidity in sulfate melts, one should mention the study⁵⁵ in which the potentiometric titration of MoO_3 , $Cr_2O_7^{2-}$, PO_3^{3-} , $P_2O_7^{4-}$, and V_2O_5 with sodium carbonate in the K_2SO_4 – Li_2SO_4 – Na_2SO_4 melt was achieved at 625 °C. The e.m.f. jump was observed at an acid : carbonate molar ratio of 1 : 1. In the case of vanadium oxide, the ratio was 1 : 3. There is no information about the equilibrium constant.

5. Silicate melts

The studies of silicate melts are as a rule of applied importance and these systems are widely used in industry (slags, glasses, *etc.*).

A number of studies^{56–58} have been devoted to the dependence of the acidity of silicate melts on their composition. Together with SiO_4^{4-} , the polyanions $(SiO_3)_3^{6-}$ and $(SiO_{2.5})_6^{6-}$ exist in the PbO – SiO_2 system ($N_{SiO_2} = 0$ – 0.6) at 1100–1200 °C.⁵⁶ A decrease in the ratio Na_2O/SiO_2 in fused glasses diminishes the basicity, whereas magnesium oxide hardly affects the basicity of the melt.⁵⁷ The study was carried out with the aid of the $Ag(O_2)$ oxygen electrode in concentration cells.

The platinum oxygen electrode is satisfactorily reversible in the PbO – SiO_2 , Na_2O – CaO – SiO_2 , and MO – PbO – SiO_2 silicate melts, where M is an alkali earth metal cation.⁵⁹

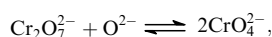
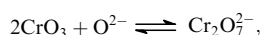
The application of the membrane oxygen electrode for the monitoring of the acidity of fused silicates during glass making has been described.⁶⁰ The study of the basicity of Na_2O – Al_2O_3 – SiO_2 melts by an e.m.f. method showed that Al_2O_3 exhibits weaker acid properties than SiO_2 .⁶¹

Under the conditions of the corrosion of the glasses $Na_2O \cdot x \cdot Al_2O_3 \cdot 2SiO_2$ ($x = 0$ – 0.4) in alkaline earth metal nitrate melts, the degree of interaction of the melt with the silicate increases with decrease in the radius of the alkaline earth metal cation, *i.e.* with intensification of its acidity.⁶²

The influence of the charge and radius of the cation in the oxides Tl_2O , PbO , CdO , ZnO , and Bi_2O_3 on the basicity of the lead metasilicate melt has been investigated potentiometrically at 800, 850, and 900 °C.⁶³

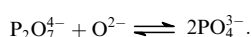
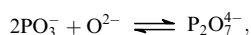
6. The equimolar KCl–NaCl mixture

The reversibility of the oxygen gas electrode $Pt(O_2)$ in chloride melts has been investigated and the constants for the acid–base equilibria involving chromium(VI), molybdenum(VI), and tungsten(VI) oxides and anions have been determined at 700 °C.^{64–69} The constants for the addition of the oxide ion to chromium oxide and sodium metaphosphate have been found.^{64–66} It has been established that the titration of CrO_3 proceeds in accordance with the scheme



and the equilibrium constant is 2.88×10^3 for the first stage and 1.4×10^{-1} for the second.

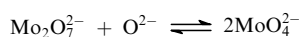
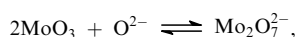
The metaphosphate ions are also titrated in two stages:



The equilibrium constants for the first and second stages are $(2.88 \pm 1.2) \times 10^3$ and $(2.5 \pm 1.4) \times 10$ respectively.

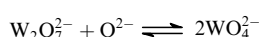
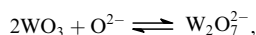
An excess of the titrant (O^{2-}) leads to the formation of basic phosphates, to which the authors attribute the composition $\text{PO}_3^- \cdot 2\text{O}^{2-}$. When sodium carbonate is used as the titrant, basic products are not formed. The Ba^{2+} and Li^+ cations exhibit appreciable acid properties in a chloride melt; the equilibrium constants for the addition of the oxide ion are 8.1×10^3 and 3.53×10^2 respectively.

The study of the acid properties of MoO_3 and the corresponding anions showed that the equilibrium constants for the addition of the oxide ion, *i.e.*

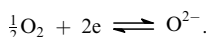


are 5×10^4 and 880 ± 880 respectively.⁶⁷

Two studies^{68,69} were devoted to the determination of the constants of the acid–base equilibria involving a tungsten(VI) oxo-compound. The titration of tungsten oxide in the melt is also a two-stage process:

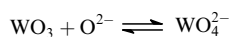


with the equilibrium constants 1460 ± 390 and 880 ± 880 respectively. The platinum oxygen electrode exhibits a satisfactory reversibility with respect to oxide ions in a chloride melt.⁶⁹ The slope of the E – $p\text{O}$ relation is close to $2.3RT/2F$ (F is the Faraday), which corresponds to the electrode process



The above results served as the basis for further electrochemical studies on electrochemical reduction reactions of Group VI metals.^{70–72} The theoretical foundations and principles of controlling electrochemical processes involving the isolation of metals and their compounds with nonmetals (carbides, borides, silicides) from ionic melts have been developed.⁷³

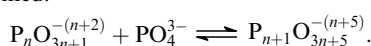
In a study of the acid–base equilibria in CaWO_4 solutions, the solubility of CaO in the KCl – NaCl melts at 1000 K was found to be ~ 0.084 mol.%.⁷⁴ The solubility of scheelite in a chloride melt at 1000 K is $10^{-3.5}$ mol kg^{-1} . The equilibrium constant for the reaction



is ~ 10 .

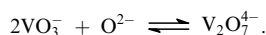
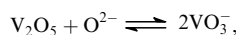
According to Combes and Tremillon,⁷⁴ the polyanion $\text{W}_3\text{O}_{10}^{2-}$ ($pK = 12.7$) is formed on reverse titration. Thus the titration curve is not reversible. The results may be accounted for by the elimination of WO_3 from acid chloride melts in the form of the oxide chloride. Under the conditions of reverse titration, the substance used as the titrant is lost in an uncontrolled manner. These considerations apply also to other studies in which titration involving the transition from a base to an acid was resorted to in the investigation of the acid properties of the oxo-compounds of Group VI elements.

The acid–base equilibria in solutions of phosphorus(V) oxo-compounds have been investigated at 700 °C with the aid of the membrane oxygen electrode $\text{Pt}(\text{O}_2)|\text{ZrO}_2(\text{Y}_2\text{O}_3)$.⁷⁵ In the melt with the ratio $\text{Na}_2\text{O}:\text{P}_2\text{O}_5 = 1.67-3$, the polyphosphate ions are formed:



The corresponding equilibrium constants have been determined. The solubilities of the polyphosphates formed have been found by the cryoscopic method.

The titration of V_2O_5 takes place in two stages:⁷⁶



The pK for the first and second stages are -9.3 ± 0.3 and -8.3 ± 0.3 respectively.

The acid–base properties of certain higher oxides and oxo-anions in chloride melts at 700 °C have been investigated in a series of studies.^{77–81} The results, presented in Table 1, agree satisfactorily with the analogous data obtained with the aid of the membrane oxygen electrode $\text{Pt}(\text{O}_2)|\text{ZrO}_2$. The application of the platinum oxygen electrode leads to pK values which are lower by approximately 3–4 orders of magnitude. In chloride melts, the $\text{Cr}_2\text{O}_7^{2-}$ ion is unstable and decomposes with formation of equimolar amounts of CrO_3 and CrO_4^{2-} .⁷⁹

Table 1. The constants of certain acid–base equilibria in KCl – NaCl and NaI melts.^{77–81}

Equilibrium	– pK		
	m^a	N^b	mol. %
KCl–NaCl melt, 700 °C			
$2\text{PO}_3^- + \text{O}^{2-} \rightleftharpoons \text{P}_2\text{O}_7^{4-}$	8.01 ± 0.1	10.67	6.67
$\text{PO}_3^- + \text{O}^{2-} \rightleftharpoons \text{PO}_4^{3-}$	5.93 ± 0.1	7.26	5.26
$\text{PO}_3^- + 2\text{O}^{2-} \rightleftharpoons \text{PO}_5^{5-}$	7.24 ± 0.1		
$\text{CrO}_3 + 2\text{O}^{2-} \rightleftharpoons \text{CrO}_5^{4-}$	8.41 ± 0.1	9.77	7.77
$\text{Cr}_2\text{O}_7^{2-} + \text{O}^{2-} \rightleftharpoons 2\text{CrO}_4^{2-}$	7.18 ± 0.1	7.18	7.18
$2\text{CrO}_4^{2-} + \text{O}^{2-} \rightleftharpoons \text{Cr}_2\text{O}_6^{6-}$	1.60 ± 0.2	4.26	0.26
$\text{MoO}_3 + \text{O}^{2-} \rightleftharpoons \text{MoO}_4^{2-}$	8.32 ± 0.2	9.65	7.65
$\text{MoO}_3 + 2\text{O}^{2-} \rightleftharpoons \text{MoO}_5^{4-}$	9.71 ± 0.3	11.37	7.37
$\text{WO}_3 + \text{O}^{2-} \rightleftharpoons \text{WO}_4^{2-}$	9.31 ± 0.2	10.64	8.64
$\text{WO}_3 + 2\text{O}^{2-} \rightleftharpoons \text{WO}_5^{4-}$	10.67 ± 0.5	13.33	9.33
$\text{B}_4\text{O}_7^{2-} + \text{O}^{2-} \rightleftharpoons 4\text{BO}_2^-$	4.82 ± 0.1	2.16	4.16
$\text{BO}_2^- + \text{O}^{2-} \rightleftharpoons \text{BO}_3^{3-}$	2.37 ± 0.2	3.17	1.70
$\text{V}_2\text{O}_5 + \text{O}^{2-} \rightleftharpoons 2\text{VO}_3^-$	6.95 ± 0.2	6.95	6.95
$\text{V}_2\text{O}_5 + 2\text{O}^{2-} \rightleftharpoons \text{V}_2\text{O}_7^{4-}$	12.23 ± 0.1	14.89	10.96
$\text{V}_2\text{O}_5 + 3\text{O}^{2-} \rightleftharpoons 2\text{VO}_4^{3-}$	12.30 ± 0.1	14.96	10.96
$\text{V}_2\text{O}_5 + 5\text{O}^{2-} \rightleftharpoons 2\text{VO}_5^{3-}$	13.88 ± 0.5	19.20	11.20
$2\text{GeO}_2 + \text{O}^{2-} \rightleftharpoons \text{Ge}_2\text{O}_5^{2-}$	4.18 ± 0.4	6.84	2.84
NaI melt, 700 °C			
$2\text{VO}_3^- + \text{O}^{2-} \rightleftharpoons \text{V}_2\text{O}_7^{4-}$	5.40 ± 0.3	7.10	4.10
$\text{V}_2\text{O}_7^{4-} + \text{O}^{2-} \rightleftharpoons 2\text{VO}_4^{3-}$	1.68 ± 0.3	1.68	1.68
$\text{B}_4\text{O}_7^{2-} + \text{O}^{2-} \rightleftharpoons 4\text{BO}_2^-$	5.02 ± 0.8	3.37	5.37

^a In units of molality. ^b In units of normality.

7. Other alkali metal halide melts

Empirical acidity series in KCl and CsI melts at 700 °C have been quoted.^{6,7} The practical value of these studies is that the $\text{SO}_4^{2-}/\text{S}_2\text{O}_8^{2-}$, $\text{WO}_4^{2-}/\text{W}_2\text{O}_7^{2-}$, and $\text{PO}_4^{3-}/\text{P}_2\text{O}_7^{4-}$ buffer solutions proposed by the authors, which have satisfactorily reproducible $p\text{O}$ values, may be used as standard solutions for the calibration of oxygen electrodes in alkali metal halide melts.

The acidity series in the sodium iodide melt at 700 °C have been constructed by Rybkin and Banik.⁸ The authors conclusion that the carbonate and hydroxide ions are bases of equal strength cannot be regarded as correct, since the acidity scales were constructed using solutions in which the contents of the test reagents were the same (0.01 mol kg^{-1}), whereas it follows from the equations



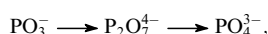
that the amount of hydroxide should be twice as great. One mole of O^{2-} may be formed from 1 mol of CO_3^{2-} , whereas only 0.5 mol of O^{2-} may be obtained from 1 mol of OH^- . Indeed, in another study by the same workers it was shown that the hydroxide ion is a stronger base than the carbonate.⁸²

Certain results of the study of the acid properties of boron(III) and vanadium(V) oxo-compounds in the NaI melt at 700 °C, carried out by Cherginets,⁸¹ are presented in Table 1.

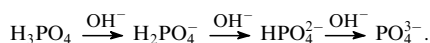
The comparative Lux–Flood base strengths (OH^- , CO_3^{2-} , SO_4^{2-} in the NaI melt at 700 °C have been established by titration with sodium pyrophosphate.^{82,83} The first of these bases reacts with the acid in proportions of 2:1, whilst the others are neutralised in proportions of 1:1. Depending on the e.m.f. jump at the point of equivalence, the bases investigated can be arranged in the sequence $\text{OH}^- > \text{CO}_3^{2-} > \text{SO}_4^{2-}$ in terms of the decrease in basicity. The equilibrium constants have not been quoted.

In a number of instances, the substances introduced into the melt actually exist in the latter in another form. For example, potassium nitrate and nitrite decompose to the oxides at the experimental temperature.^{6,7}

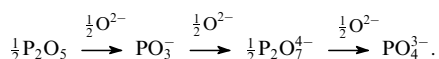
This applies also to pyro- and per-sulfates^{6,7} and also to acid phosphates.⁸ The acidity of the pyrophosphate in an iodide melt is much higher than that of the metaphosphate ion according to the data of Rybkin and Banik.⁸ However, the titration of phosphorus oxo-compounds proceeds in accordance with the scheme



and the acidity of the pyrophosphate should therefore be lower, because in the conjugate pair ‘metaphosphate–pyrophosphate’ the latter is the base. The frequently observed lack of correlation between the pH of aqueous solutions of salts and the pO of the analogous solutions in the melt (this usually applies to phosphorus oxo-compounds) is due to the difference between the processes occurring during neutralisation. The neutralisation of phosphoric acid in aqueous solutions proceeds in stages in accordance with the scheme



The analogous sequence in melts assumes the form

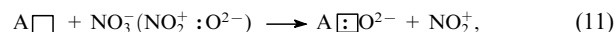


A correlation should therefore be sought between the acidities of an aqueous solution of the anion and a solution of the corresponding anhydro-acid in the melt. The salts NaPO_3 and $\text{Na}_4\text{P}_2\text{O}_7$ can be readily obtained by pyrolysing the corresponding acid salts, but the reverse processes hardly occur in aqueous solutions and the above substances exist as the salts of the independent acids HPO_3 and $\text{H}_4\text{P}_2\text{O}_7$. On the other hand, in the case of meta- and pyro-arsenates, which exhibit a greater tendency to hydrolyse, a correlation between the pH of the aqueous solutions of these anhydro-compounds and the pO of the solutions in the melt should be observed. Thus the breakdown of the correlation in the case of phosphorus oxo-compounds is only apparent, because it is induced solely by kinetic limitations.

Analysis of literature data makes it possible to discover also a fundamental inaccuracy which has arisen in the studies of oxo-acidity in nitrate melts, in particular in KNO_3 . As a constituent of this melt, the NO_3^- ion is capable of dissociating with formation of O^{2-} in accordance with the equation



which is thus the equation of the intrinsic acid–base dissociation of the solvent.⁸⁴ In the potassium nitrate melt, there is a possibility of the levelling off of both acid properties,^{84 i.e.}

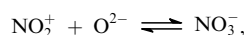


and basic properties (as has been observed by De Andrade *et al.*),^{85 i.e.}



This implies that acids stronger than NO_2^+ and bases stronger than K_2O cannot exist. According to Eqn (11), the acid–base titration curves for solutions of strong acids of equal concentration should be identical. This permits a fresh look at the results obtained in earlier studies.^{39–42}

We shall consider the potentiometric titration data for solutions of oxo-acids (Fig. 1). The curves presented virtually coincide (despite some difference between the initial concentrations of the acid). This means that the process



occurred in all cases, whereas the above investigators^{39–42} performed their calculations on the basis of reaction equations with other stoichiometric coefficients, which in fact led to an appreciable drift in the calculated equilibrium constants.

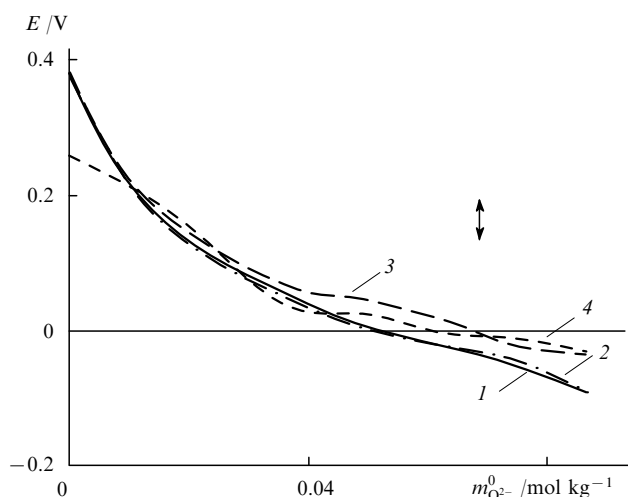


Figure 1. Potentiometric titration curves for solutions of the oxo-acids CrO_3 (1), MoO_3 (2), WO_3 (3), and PO_3 (4) at concentrations of $\sim 0.1 \text{ mol kg}^{-1}$ in the KNO_3 melt at 350 °C (according to data in Refs 39–42). The arrow indicates the error in the measurement of the e.m.f.

The levelling of the acid strengths in oxygen-containing melts makes the latter an unsuitable medium for the determination of the equilibrium constants for processes involving strong acids. The melts of alkali metal halides, in which this phenomenon is not observed, are more suitable for this purpose. Since the physicochemical properties of ionic melts (ionic densities, charges, and radii)[†] are usually similar, the application of the acidity scale obtained for one melt in order to characterise another melt is more justified than, for example, the use of different low-temperature molecular solvents, the physicochemical properties of which (relative permittivity, donor–acceptor properties) differ extremely significantly.

[†] The radii of the NO_3^- and Cl^- ions are 0.165 and 0.167 nm respectively.¹⁰

III. The solubilities of oxides in alkali metal halide melts

The dissolution of oxides in alkali metal halide melts is accompanied by the interaction of the ions of the oxides with those of the melt (solvation). These interactions are superimposed on the oxide dissociation process and lead to the formation of halo-complexes and oxides of the alkali metals. Furthermore, part of the molecular oxide also dissolves. Thus the following equilibria are established in a saturated solution of the oxide:



where Kt^+ is the cation of the melt (Cs^+ , K^+ , and Na^+).

Since the formation of complexes between the anions of the melt and various cations proceeds to approximately the same extent, one may postulate that the dependence of the solubility of the oxide on the nature of its constituent metal is determined primarily by the degree of interaction of the metal cation and the oxide ions in the melt, which is an acid–base process as defined by Lux and Flood.

According to Lux and Flood, the equilibrium constant of reaction (1) may serve as a quantitative measure of the acidity of the chemical compound or ion. If all the participants of this reaction are in the dissolved state, then the equilibrium established in the homogeneous system may be regarded as of the acid–base type. However, the solubility of the majority of oxides in melts is limited (the excess oxide precipitates). Thus, the oxide ions are eliminated from the melt not only as a result of the reaction with the cationic acid but also as a result of the formation of another phase (*i.e.* a deposit of the oxide). In the study of the solubilities of oxides in melts by potentiometric titration, one must therefore take into account equilibrium (13). It follows from Eqns (13)–(16) that the binding of the oxide ions by the metal cations is in general a heterogeneous process, as a result of which a new phase (the metal oxide) is formed. In this case, the affinity of the cation M^{2+} cannot be unambiguously related to the completion of the $\text{M}^{2+} + \text{O}^{2-}$ interaction in the melts. The solubility of the oxide (Σs_{MO}) in the melt can be determined, taking into account its incomplete dissociation, as the sum of the activities (concentrations) of the metal cations and the undissociated oxide:

$$\Sigma s_{\text{MO}} = a_{\text{M}^{2+}} + a_{\text{MO}}, \quad (17)$$

where $a_{\text{M}^{2+}}$ and a_{MO} are respectively the activity of the metal cation and of the undissociated oxide in the saturated solution.

Since the concentration of the undissociated oxide in the saturated solution is as a rule extremely difficult to determine, in practice the solubility product P_{MO} is used as the characteristic of the solubility of the oxide:

$$P_{\text{MO}} = a_{\text{M}^{2+}} a_{\text{O}^{2-}}. \quad (18)$$

According to the Law of Mass Action, in the region of saturation of the solution the dissociation constant of the oxide can be expressed in the form

$$K_{\text{MO}} = \frac{a_{\text{M}^{2+}} a_{\text{O}^{2-}}}{a_{\text{MO}}}. \quad (19)$$

Comparison of Eqns (18) and (19) leads to the expression

$$K_{\text{MO}} = \frac{P_{\text{MO}}}{a_{\text{MO}}}. \quad (20)$$

The complete set of the constants characterising the equilibria in the saturated solution of the oxide can be obtained, provided that two parameters of Eqn (20) out of three have been found.

Owing to the lack of well developed and generally accepted methods for the determination of activity coefficients and their dependence on the concentrations of the corresponding species in fused salts, in practice the calculation of concentration parameters is usually resorted to.

1. Methods for the investigation of the solubilities of oxides in melts

In the study of the solubilities of oxides in oxygen-containing and halide melts, different versions of the isothermal saturation and potentiometric titration methods are usually employed.

The isothermal saturation method consists in the successive addition of the test oxide to the solvent melt until the formation of a saturated solution. The instant of saturation is established both with the aid of potentiometric measurements^{85,86} and by a titrimetric procedure (by determining the concentration of the metal forming the oxide in a sample of the melt).⁸⁷ The final result is the determination of the ‘total’ solubility in accordance with Eqn (17), which, when account is taken of Eqns (18) and (20), may be expressed in the form

$$\Sigma s_{\text{MO}} = P_{\text{MO}}^{1/2} + \frac{P_{\text{MO}}}{K_{\text{MO}}}. \quad (21)$$

Naturally, if the potentiometric method with a precalibrated electrode system is used to monitor the degree of saturation, then, knowing the amount of added oxide and the equilibrium molality of the oxide ion in the melt, the parameters of its dissociation can be determined separately. However, this case is more of an exception. Furthermore, in order to obtain a representative selection it is necessary to carry out a series of experiments, which requires much time and a considerable expenditure of reagents.

The method involving the analysis of melt samples⁸⁷ is used fairly widely, but it may lead to distortion of the results as a consequence of the contamination of the sample by suspended oxide particles. It is therefore necessary to take measures to prevent the formation of suspensions in the melt, which greatly complicates the technique of the measurement.

The isothermal saturation method is very convenient in studies over a range of temperatures, but it can hardly be used to determine the solubilities of oxides of the type MgO , NiO , Al_2O_3 , *etc.*, which are extremely sparingly soluble in nitrate and halide melts. As a rule, the data obtained in such investigations do not permit the simultaneous estimation of the solubility product of the oxide and its dissociation constant with the exception of limiting cases where the oxide is either fully dissociated or, conversely, is hardly dissociated. Since the ‘pure’ melt itself contains oxide ions, in the determination of the solubility errors may arise which become especially pronounced if the solubility is comparable to the concentrations of the oxide ion in the ‘pure’ solvent melt.

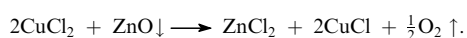
The potentiometric titration method is applicable over a much wider range. It makes it possible to determine the solubility product and in many instances (when an unsaturated solution region is present on the titration curve) also to calculate the dissociation constants of oxides in melts. Potentiometric studies are as a rule carried out in cells with transport, but this does not lead to significant experimental errors, because the potentials of liquid compounds in melts are insignificant.⁸⁸

2. The KCl–LiCl melt (0.405 : 0.595)

The solubility of the Fe(II, III) oxides in the KCl–LiCl (0.405 : 0.595) melt has been investigated.^{89,90} Potentiometric and diffractometric studies showed that, on precipitation by the donor of oxide ions (CO_3^{2-} , pure FeO is formed, whereas trivalent iron is deposited as the LiFeO_2 – $\text{Li}_y\text{Fe}_{1-y}\text{O}$ solid solution. The solubility products of the iron oxides FeO, Fe_3O_4 , and Fe_2O_3 are $10^{-5.4}$, $10^{-36.3}$, and $10^{-29.16}$ respectively. The Fe^{3+} cations oxidise the chloride melt with liberation of chlorine. An evident disadvantage of these studies is the use of sodium carbonate,

known *a priori* to be incompletely dissociated, as the base, which undoubtedly influenced the calculated solubility products. Furthermore, it is not comprehensible how it was possible to obtain Fe_2O_3 by deposition if the corresponding cation is unstable in the chloride melt.

The qualitative study of the solubilities of oxides in the KCl – LiCl melt at $\sim 500^\circ\text{C}$ was based on the visual monitoring of the solubility.^{91,92} KOH was added to a solution of the chloride of the test metal in the melt. If the oxide was not then precipitated, it was regarded as soluble (CdO , PbO , BaO , CaO , Ag_2O). Otherwise the oxide was regarded as sparingly soluble (CoO , NiO , ZnO) or insoluble (MgO , BeO , Al_2O_3). Copper(II) oxide proved to be unstable in chloride melts and its dissolution was accompanied by the reduction of Cu^{2+} ions to Cu^+ . The chlorides of certain other metals in the highest oxidation states, for example TiCl_3 , FeCl_3 , and AuCl_3 , behave similarly. The addition of the corresponding metal chlorides to a melt containing other oxides led to the dissolution of the latter as a result of the occurrence of reactions of the type



A significant difference between the solubilities of the oxide in 'the powder form' or prepared *in situ*, i.e. by adding KOH to a solution of the corresponding chloride, has been noted. The solubilities of CaO and CdO obtained by the latter method are much higher.

Saturated solutions of various oxides have been investigated polarographically.^{93,94} The degree of interaction of the oxide with the melt was inferred from the potential, the shift of the polarogram, and the change in its form compared with theoretical data. It has been established that, in the electrochemical reduction of a cation, the stage involving the acid–base dissociation of the corresponding oxide is rate-limiting. The stability constants of the oxides were found to have the following values (in mol.%): $\text{CoO} - (9.9 \pm 1.9) \times 10^3$, $\text{NiO} - (6.8 \pm 0.8) \times 10^3$, $\text{PbO} - (3.4 \pm 1.3) \times 10^3$, and $\text{Bi}_2\text{O}_3 - (8.7 \pm 3.5) \times 10^3$. The equilibrium constant for the formation of the plumbate ion from PbO is $(2.0 \pm 1.6) \times 10^2$. Cadmium, copper, and silver oxides were fully dissociated under the experimental conditions, which agrees with other data.^{91,92}

The estimation of the solubilities of a series of oxides was undertaken in order to elucidate the possibility of using the corresponding metal oxide electrodes (electrodes of the second kind) as indicator oxygen electrodes.⁹⁵ The solubilities of the oxides at 500°C were found to have the following values (in mol kg^{-1}): $\text{NiO} - 3.3 \times 10^{-4}$, $\text{BiOCl} - 6.8 \times 10^{-4}$, $\text{PdO} - 9.4 \times 10^{-3}$, $\text{PtO} - 3.32 \times 10^{-2}$, and $\text{Cu}_2\text{O} - 3.8 \times 10^{-2}$.

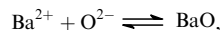
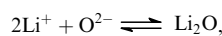
3. The KCl – NaCl melt (0.50 : 0.50)

The study of the solubilities of CaO , SrO , and BaO over the range of temperatures from T_m to 900°C was carried out by an isotopic method.⁹⁶ Together with the KCl – NaCl melt, the pure individual potassium and sodium chlorides were also used as the solvent. The solubilities of the oxides increased in the sequence $\text{CaO} < \text{SrO} < \text{BaO}$. The solubility products of the oxides in the KCl and KCl – NaCl melts were found to be similar and somewhat lower than in the NaCl melt. Comparison of the experimental data with the results of thermodynamic calculations showed that the solution contains simultaneously both the molecular oxide MO and the M^{2+} and O^{2-} ions formed on its dissociation.

In an analogous investigation,⁸⁷ the solubilities of the oxides in the temperature range 700 – 810°C were determined by measuring the concentrations of the metal cations in the solidified melt specimen using the complexometric titration method. Comparison of the observed solubility products with theoretical estimates made it possible to calculate the activity coefficients of the oxide ions in the saturated solutions studied. The quantities obtained can hardly be regarded as correct, because they are influenced significantly by the incomplete dissociation of the oxides in the melt and by the deviations from ideality of the solution induced by

the presence of doubly charged alkaline earth metal cations and O^{2-} . The contribution of each of these components was not estimated separately.

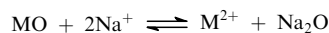
The acid properties of the Ca^{2+} , Li^+ , and Ba^{2+} cations have been investigated⁹⁷ at 700°C and the constants for the acid–base equilibria



were found as 353 mol.% and 81 mol.% respectively. It follows from these data that all the cations investigated are appreciably acid.

The acidity of the cations of the main subgroup elements weakens with increase in the atomic number of the element, whereas in the Group B elements and in transition series such behaviour is not observed.⁹ Careful analysis of the data of Ovsyannikova and Rybkin⁹ showed, however, that the weakening of the acid properties occurs also in the Zn – Cd diad. Although the above study can in fact be regarded as systematic, it is difficult to extract from it any quantitative data for the estimation of the solubilities of the oxides, since the additional equilibrium (7) is superimposed on the main acid–base equilibrium (14) in the KCl – NaCl melt, because all the cations investigated were added to the melt in the form of sulfates and the influence of this equilibrium was not estimated quantitatively. The use of sulfates should evidently lead to the formation of a deposit and the evolution of SO_3 from the solutions containing the most acid cations.

Furthermore, the results of the above workers⁹ are in direct conflict with the phenomenon of the levelling of basic properties described in the preceding section. According to potentiometric data, the content of O^{2-} at equilibrium in the BaSO_4 solution is ten times higher than in the K_2SO_4 and Na_2SO_4 solutions at the same concentration. The concentrations were found to be higher to a somewhat lesser extent in solutions containing Cs^+ (by a factor of 3.2), Sr^{2+} (by a factor of 2), and Rb^+ (by a factor of 1.2). It follows from the equation

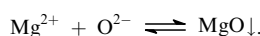


that, when the metal cation in the melt based on sodium salts is a weaker acid than Na^+ , the equilibrium should be displaced to the right and the basicity of O^{2-} is limited by the basicity of Na_2O in the corresponding melt. The addition to the melt of a small amount of a compound with cations less acid than Na^+ should therefore induce the same effect as the addition of an equivalent amount of the corresponding sodium salt (since the authors investigated solutions at a concentration of 0.01 mol kg^{-1} , $\text{M}^{n+}/\text{Na} = 0.0026/n$). However, the results obtained in the above study⁹ conflict with this conclusion.

The solubilities of ZnO , HgO , NiO , and SrO have been investigated by the potentiometric titration method, with the initial transition from the acid to the base and then from the base to the acid.⁹⁸ The characteristics corresponding to the solubility product and the dissociation constant were calculated from the experimental data. Unfortunately the average values of the calculated parameters of the equilibria are not quoted in the above study⁹⁸ (the averaging was carried out by Combes *et al.*⁹⁹). It was found that the calculated values of K_{MO} and P_{MO} for the forward and reverse titrations differ significantly. This constitutes yet another piece of evidence in support of the need to apply a single research technique in the search for correlations. In the sequence $\text{MgO} < \text{NiO} < \text{ZnO} < \text{SrO}$, the solubility increases. In a later study,⁹ a somewhat different series of cations was found. However, preference should be given to the results obtained by the potentiometric titration method.

The solubilities of a series of oxides in the KCl – NaCl melt at 1000 K have been investigated also in other studies.^{85,99–101} Two steps were observed on the Mg^{2+} titration curve: the first corresponded to the formation of Mg_2O^{2+} and the second to the

formation of MgO.⁹⁹ Although the potentiometric studies of the solubilities of MgO in this and analogous chloride melts have been frequently performed, no one else observed a similar phenomenon. There is usually only one e.m.f. jump, corresponding to the reaction



The use of BaO for the titration of alkaline earth metal cations cannot be regarded as correct either, because in this case the substances precipitated are not the individual oxides but their solid solutions with BaO, the solubility of which differs from that of the pure oxide. The principal result of the studies quoted is the conclusion that the solubilities of the oxides increase in the series of alkaline earth metals $\text{MgO} < \text{CaO} < \text{BaO}$ (the solubility of MgO was measured by the potentiometric method and those of the remaining two oxides were found by the isothermal saturation method). The temperature dependence of the solubility of zirconium(IV) oxide in the KCl–NaCl melt assumes the form¹⁰²

$$N_{\text{ZrO}_2} = (-5.7 \pm 3.1) \times 10^{-6} + (7 \pm 3) \times 10^{-9} T.$$

The solubility of ZrO_2 at 700 °C is insignificant even in an acid medium, so that the use of membrane electrodes based on stabilised ZrO_2 should not lead to an appreciable contamination of the test melt by zirconium(IV) compounds.

The solubilities of 11 oxides of s^2 and $3d$ metals at 700 °C have been investigated (Table 2)^{103, 104} The existence of a correlation between the solubilities of the oxides and the crystal-chemical radii of the cations r was established:

$$\text{p}P_{\text{MO}} = \text{p}P_{r \rightarrow \infty} + \frac{k}{r^2}. \quad (22)$$

In a number of instances, the results obtained by different workers^{98–101, 103, 104} agree well with one another, which can be accounted for by the virtually identical experimental conditions (the method for the determination of the solubility, the titrant, the molality of the cation, *etc.*). However, the discrepancies are usually fairly considerable. Such a scatter of the results has not so far been accounted for and the impossibility of a systematic treatment of the results naturally did not promote the development of studies on the solubilities of oxides in alkali metal halide melts.

Solubility data can be divided into two groups depending on the method for their determination (Fig. 2); within each group, the solubilities of one oxide have similar values. A fairly unexpected result of the comparison of the available literature data is the conclusion that the solubilities of oxides found by the isothermal saturation method are as a rule several orders of magnitude lower than the values calculated from potentiometric data, although in the former case one determines Σs_{MO} and in the latter only s_{M}^{2+} .

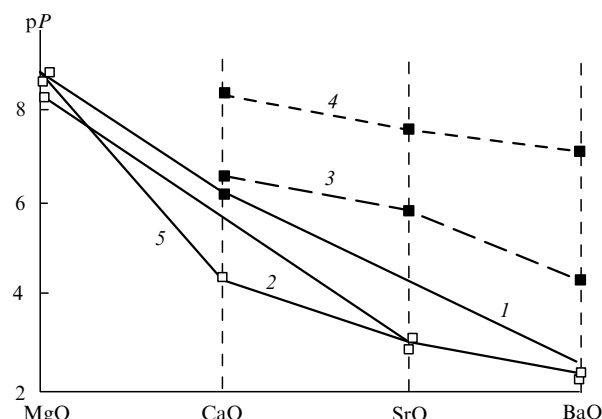


Figure 2. The solubilities of alkaline earth metal oxides in the KCl–NaCl melt measured by the isothermal saturation (open squares) and potentiometric titration (filled squares) methods: (1) according to the data of Combes and coworkers;^{85, 99–101} (2) according to the data of Delimarskii *et al.*;⁹⁸ (3) according to the data of Shapoval and Tsiklauri;⁹⁷ (4) according to Volkovich's data;⁸⁷ (5) according to the data of Cherginets and coworkers^{104, 110} (at 700 °C).

The higher solubility in melts of oxides prepared *in situ* was first noted by Delarue,^{91, 92} although no explanation of the results was given.

The solubility of any substance depends on the size of its crystals in contact with the solution. For substances dissolving in the form of molecules, this dependence is expressed by the Ostwald–Freundlich formula:¹⁰⁵

$$\frac{RT}{M} \ln \frac{S_1}{S_2} = \frac{2\sigma}{d} \left(\frac{1}{r_2} - \frac{1}{r_1} \right),$$

where S_1 and S_2 are the solubilities of the crystals with the radii r_1 and r_2 respectively, M is the molecular weight, d the density, and σ the surface energy.

For dissociating substances, the analogous equation assumes the form

$$\frac{RT}{M} \ln \frac{P_1}{P_2} = \frac{2\sigma}{d} \left(\frac{1}{r_2} - \frac{1}{r_1} \right),$$

where P_1 and P_2 are the corresponding solubility products.

In particular, it follows from the equations presented that an increase in crystal size leads to a diminution of solubility. For this reason, larger particles should be deposited from concentrated solutions than from dilute solutions. The increase in the size of crystals in a concentrated solution of the cation can be explained

Table 2. The values of $\text{p}P_{\text{MO}}$ and $\text{p}K_{\text{MO}}$ for certain oxides in alkali metal halide melts (on the mole fraction scale).^{103, 104}

Oxide	KCl–NaCl (700 °C)		CsCl–KCl–NaCl (600 °C)		CsCl–KCl–NaCl (700 °C)		CsBr–KBr (700 °C)		CsI (700 °C)
	pP	pK	pP	pK	pP	pK	pP	pK	pP
BaO	4.66		4.75		~4.5		5.16		4.98
SrO	5.44	2.30	5.81	2.71	5.54	2.14	6.82	2.45	6.28
CaO	6.72		7.73	3.71	6.86	2.99	9.93	3.76	7.50
MgO	11.62		12.68		11.68		12.76		
MnO	9.13		9.73		9.49		10.70		
CoO	10.24		10.92		10.50		11.33		
NiO	11.38		12.60		11.42		12.71		
Cu ₂ O	6.53		6.95	3.29	6.35	2.59			
ZnO	9.28		8.80		8.15		11.03		
CdO	7.35		7.54		7.09		9.35		8.00
PbO	7.47	4.47	8.21	5.08	7.04	4.03	8.52	5.81	7.80

by the ageing of the oxide — recrystallisation, which is faster when the concentrations of the reactants increase.

Under the conditions of oxidative titration, a finely dispersed metal oxide is formed and begins to 'age' as a consequence of the occurrence of recrystallisation, *i.e.* of the increase in the size of the crystals and the decrease in the surface energy σS , which leads to a decrease in solubility (solubility products). The recrystallisation is promoted by prolonged maintenance at a high temperature and for a high concentration of the corresponding ions in solution. The first case obtains, in particular, when studies are performed by the isothermal saturation method, where the oxide is subjected to preliminary heat treatment or sintering and the pellets obtained are kept in the melt for several hours. In the second case, the transfer of the substance from small to large crystals is evidently accelerated.

We may note that the solubilities of the oxides quoted by Delimarskii *et al.*⁹⁸ are somewhat higher than those obtained by the present author. This can apparently be accounted for by the fact that the study of Delimarskii *et al.*⁹⁸ was carried out in more dilute solutions (0.01 mol kg⁻¹), where ageing is somewhat slower. A significant disadvantage of dilute solutions is the very marked change in the concentration of the cation during the period of the investigation and hence the poor reproducibility of the results. The measurement of the solubility of NiO in the KCl–NaCl melt may serve as an example. Titration of a solution at a concentration of 0.01 mol kg⁻¹ yields $pP_{\text{NiO}} = 7.95 \pm 0.20$ (Delimarskii *et al.*⁹⁸ obtained 8.32), whereas at a concentration of 0.05 mol kg⁻¹ we have $pP_{\text{NiO}} = 9.03 \pm 0.06$. However, in this case too the values of pP differ by an order of magnitude. The results quoted^{98, 101, 103, 104} for magnesium and barium oxides were obtained by titrating solutions at a concentration of 0.05 mol kg⁻¹ and they agree very well with our data. In the vicinity of the equivalence point, the values of pP_{MO} frequently decrease slightly. This is apparently also caused by the difference between the dimensions of the crystals deposited from the melt.

4. The solubilities of the oxides in other alkali metal halide melts

The solubilities of the oxides of s^2 and $3d$ metals in the CsCl–KCl–NaCl (0.455:0.245:0.30, eutectic) melt have been investigated at 600 and 700 °C (Table 2).^{106–111} A method for the separation of the regions of existence of unsaturated and saturated solutions of the oxides, ensuring that the calculated dissociation constants and solubility products of the oxides respectively are correct, has been proposed and justified. The solubilities of the oxides in lithium-free chloride melts at the same temperature are identical (in mole fractions) and the temperature variation agrees with the Schroeder equation.

The solubilities of the oxides in the 2CsBr·KBr melt at 700 °C are lower than in the analogous system with the Cl⁻ ion.^{112–114} Thus, SrO which is moderately soluble in chloride melts, becomes sparingly soluble in the bromide melt, whilst the sparingly soluble calcium and cadmium oxides become virtually insoluble. The range of oxides the solubilities of which can be investigated in the CsI melt¹¹⁵ is still narrower than in the case where systems with other halide ions are employed (Table 2). The results of the investigations have shown that the iodide melt occupies an intermediate position between the chloride and bromide melts as regards the solubilities of the oxides in it.

The linear dependence of pP on r^{-2} holds for all the alkali metal melts investigated.^{106–115} This makes it possible to employ the relations indicated (Table 3) for the estimation of the solubility products of the oxides from the cationic radii. Furthermore, on the basis of the results quoted,^{110, 111} it is possible to calculate the solubilities of the oxides also at other temperatures by means of the Schroeder equation. When one halide anion of the melt is replaced by another, the degree of association of the melt ions changes, which exerts a decisive influence on the solubilities of the oxides.

Table 3. The coefficients of Eqn (22) for alkali metal halide melts (95% confidence limits).

Melt	$T/^\circ\text{C}$	$pP_{r \rightarrow \infty}$	k
KCl–NaCl	700	1.8 ± 0.9	0.053 ± 0.01
CsCl–KCl–NaCl	600	1.7 ± 2.0	0.057 ± 0.01
CsCl–KCl–NaCl	700	1.7 ± 0.3	0.054 ± 0.02
CsBr–KBr	700	3.2 ± 1.8	0.053 ± 0.01
CsI	700	2.65 ± 0.58	0.052 ± 0.01

The study of the solubility of ZrO₂ in the potassium metaphosphate melt and in KCl–KPO₃ mixtures at 800 °C showed that the solubility of zirconium oxide reaches 1.34 mass % in pure KPO₃ and 3.25 mass % in the equimolar KCl–KPO₃ mixture.¹¹⁶ The increase in the solubility of ZrO₂ with decrease in the KPO₃ concentration is caused, according to the authors, by the depolymerisation of the latter and by the enhancement of the acid properties of the melt. At a KCl concentration above 60 mol.%, the solubility of ZrO₂ falls sharply, apparently owing to the decrease in the acidity of the melt because the intensification of the dissociation of the metaphosphate under these conditions is no longer compensated by the decrease in the concentration of the acid.

The solubilities of nickel and thorium(IV) oxides in the KF–LiF melt at 550 °C have been studied potentiometrically using a membrane oxygen electrode.^{117, 118} The solubility product of NiO is 1.3×10^{-6} , which is appreciably higher than in the chloride melt. The solubility of NiO apparently increases as a result of the formation of stable fluoride complexes of Ni²⁺.

The solubility products (in mole fractions) of Co₃O₄, NiO, and Y₂O₃ at 1100 K in the NaCl melt are $(0.99–3.3) \times 10^{-11}$, $(1.9–4.9) \times 10^{-12}$, and $(1.4–2.2) \times 10^{-36}$, while those in the Na₂SO₄ melt are $(0.8–2.2) \times 10^{-10}$, $(1.6–8) \times 10^{-11}$, and $(4.5–6.4) \times 10^{-31}$ respectively.^{119, 120} The excess titrant leads to the formation of the anionic oxo-complexes NiO₂⁻, CoO₂⁻, and YO₂⁻ in the melt.

The solubility products of zinc oxide and K₂ZnO₂ in the potassium chloride melt at 800 °C are 2.3×10^{-8} and 3.2×10^{-12} respectively.¹²¹

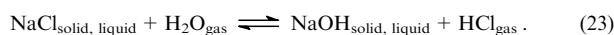
A number of studies have been devoted to oxo-acidity in alkali metal chloride melts to which cations with a high acidity have been added: MgO–BaCl₂–CaCl₂–NaCl,¹²² CaO–CaCl₂–KCl–NaCl,¹²³ CeCl₃–KCl–NaCl,¹²⁴ and ZnO–NaCl–ZnCl₂.^{125, 126} The cationic acids influence significantly the acid–base processes in ionic melts as a result of the binding of the oxide ions. This increases the solubilities of the oxides in such melts (see, for example, Refs 122 and 123).

IV. The reactions of melts with gaseous acid and basic reagents

The gases present in the atmosphere over the melt can react both with its principal components and with impurities. In reactions of the first kind, which include, in particular, hydrolysis, the gas (H₂O) behaves as a Lux–Flood base, supplying O²⁻ ions to the melt. In reactions of the second type (purification of melts by halogenating agents, dissociation of bases), the gaseous reagent is an acid.

1. High-temperature hydrolysis of melts

Reactions of this type have been investigated mainly in relation to individual alkali metal halides and their mixtures. The hydrolysis of the solid and fused sodium chloride in the temperature range 600–950 °C has been investigated by a 'dynamic method',¹²⁷ which consists in passing nitrogen, containing water vapour, through a layer of solid or fused sodium chloride:



The HCl evolved was determined titrimetrically.

The rate of evolution of HCl can be described by the following equation:

$$\frac{dn}{d\tau} = \frac{v p_{\text{HCl}}}{p}, \quad (24)$$

where p is the overall pressure, p_{HCl} the 'equilibrium' partial pressure of HCl, and v the rate of supply of the moist gas.

The equilibrium constant of reaction (23) is

$$K = \frac{\gamma^n p_{\text{HCl}}}{N p_{\text{H}_2\text{O}}}, \quad (25)$$

where γ is the activity coefficient of NaOH in NaCl. Integration of Eqn (24) taking into account Eqn (25) leads to the expression

$$n = \left[\frac{2v N p_{\text{H}_2\text{O}} K}{p\gamma} \right]^{1/2} \tau^{1/2},$$

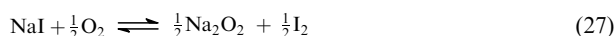
which is linear in terms of the $n-\tau^{1/2}$ variables. Evidently this relation should pass through the origin of coordinates ($\tau = 0$, $n = 0$). However, it was found that reaction (23) is complicated by the diffusion of NaOH in NaCl and the authors¹²⁷ therefore improved the model by introducing into the latter a correction λ , which is in essence the time required to reduce the diffusional limitations to a minimum:

$$n = \left[\frac{2v N p_{\text{H}_2\text{O}} K}{p\gamma} \right]^{1/2} \left\{ \tau + \lambda \left[\exp\left(-\frac{\tau}{\lambda}\right) - 1 \right] \right\}^{1/2}.$$

The hydrolysis of sodium chloride occurs to a slight extent, although the rate of evolution of HCl exceeded the expected value as a result of hydrolysis on dissolution of NaOH in NaCl.

An evident disadvantage of the above method is the use in it of the hypothesis that the partial pressure of HCl in the gas phase is equal to the equilibrium partial pressure. Judging from the experimental method, it should in fact be much lower, because NaCl is hydrolysed albeit at a low rate.

The same method has been used to investigate the high-temperature hydrolytic and oxidation reactions of sodium iodide.^{128, 129} According to the estimates made, the heats of the reactions



are 32.8 ± 2 and 13.9 ± 1 kJ mol⁻¹ for solid sodium iodide and 30.6 ± 2 and 9.3 ± 2 kJ mol⁻¹ for fused sodium iodide. Hence it follows that the latter shows a greater tendency to oxidise than to hydrolyse. In contrast to NaOH, sodium peroxide is almost insoluble in crystalline sodium iodide. The conclusions reached cannot be adopted without stipulation, because they are based on the values of ΔH and not ΔG for the reactions indicated above.

A simple but unquestionable method has been used to investigate high-temperature hydrolysis in the KCl–NaCl melt.¹⁰¹ A mixture of HCl and H₂O, obtained by passing an inert gas through aqueous HCl solutions at a definite concentration, was passed into the melt. Measurements of the equilibrium O²⁻ concentration by the potentiometric method made it possible to calculate the equilibrium constants for the process

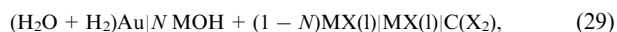


($\text{p}K = 55.3 \times 10^3 T^{-1} - 40.2$). At 1000 K, $\text{p}K \approx 15.1$ and equilibrium (28) is therefore displaced to the left.

A similar method has been used to investigate the hydrolysis of the KCl–LiCl melt at 500 °C ($\text{p}K = 9.77 \pm 0.4$).¹³⁰ The hydroly-

sis of the chloride melt is thermodynamically unfavourable and is fully suppressed in the presence of bases (at a concentration of $\sim 10^{-3}$ mol kg⁻¹).

The cells



where the symbols M and X designate the alkali metal and the halogen respectively, have been used to investigate the hydrolysis of individual alkali metal halide melts (with the exception of lithium salts).¹³¹

The e.m.f. of cell (29) is related to the concentrations of the reactants by the expression

$$E = E^0 + \frac{RT}{F} \ln \frac{P_{\text{H}_2}^{1/2} P_{\text{X}_2}^{1/2}}{P_{\text{H}_2\text{O}}} a_{\text{MOH}},$$

where P_{H_2} and P_{X_2} are the partial pressures of hydrogen and the halogen over the melt respectively.

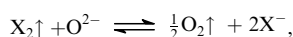
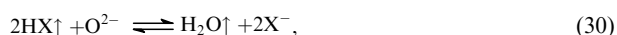
The logarithms of the equilibrium constants

$$\ln K = \frac{F}{RT} E - \frac{\Delta G_{\text{HX}}^0}{RT} + \ln \frac{P_{\text{H}_2}^{1/2} P_{\text{X}_2}^{1/2}}{P_{\text{H}_2\text{O}}} a_{\text{MOH}}$$

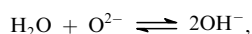
are negative, which indicates that the hydrolysis of alkali metal halide melts is thermodynamically unfavourable. The tendency towards hydrolysis of melts of individual alkali metal halides diminishes with increase in the radii of both the cation and the anion. According to the results of Smirnov *et al.*,¹³¹ the solutions of alkali metal hydroxides in the corresponding individual chlorides are close to ideality.

2. Elimination of oxygen-containing impurities from alkali metal halides

The studies of the elimination of oxygen-containing impurities from melts are as a rule of an applied character and are performed in melts having industrial applications. Various halogenating agents, usually hydrogen halides or the halogens themselves, are used to eliminate the impurities.^{132–138}



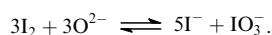
where X is the halogen. However, the water formed in reaction (30) exhibits the properties of a Lux–Flood acid, *i.e.*



and this retards the purification process. The cessation of the effect of XH may lead to partial hydrolysis, because, as can be seen from the previous section, the type (30) reactions are reversible. The shift of process (30) to the left is also promoted by the thermal instability of HBr and HI.

The effectiveness of the purification of melts based on lithium salts by hydrogen halides is much lower. Water dissolves in the KCl–LiCl melt in appreciable amounts and is firmly retained at temperatures up to 400 °C.¹³⁹ When dry HCl is passed for 1 h, H₂O is not fully removed.

The effectiveness of the purification by the halogens depends on their oxidation-reduction potentials and decreases from chlorine to iodine. In addition, the latter can disproportionate:



The iodate ions formed are stable in the melts and oxygen-containing impurities are thus not removed from the iodide melt.

The effect of ammonium halides NH₄X involves the formation of the corresponding hydrogen halide as a result of thermal dissociation.^{140–142}

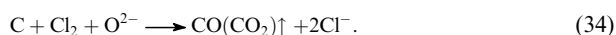
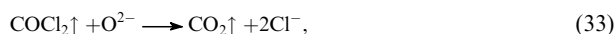
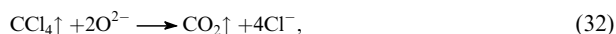


However, the addition of NH₄X is recommended only for the drying and heat treatment of the initial components and its use for

the industrial purification of the fused salts is undesirable because it is much easier to ensure the continuous supply of the corresponding hydrogen halide into the melt being purified. Ammonium halides constitute a very convenient means for the removal of oxygen-containing impurities from melts before the investigation: the addition of these crystalline salts lowers the equilibrium concentration of oxide ions to 10^{-5} – 10^{-6} mol kg $^{-1}$.¹⁰⁹

It is believed that the most convenient method for the elimination of oxygen-containing impurities from alkali metal halide melts is carbohalogenation.^{143–150}

The effectiveness of CCl₄, COCl₂, Cl₂, and the C + Cl₂ mixture (C is acetylenic carbon black) can be explained by the occurrence of the reactions¹⁴³

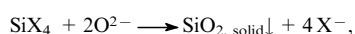


Thermodynamic analysis of reactions (32)–(34) showed that the effectiveness of the purification is in all cases approximately the same,¹⁴⁴ but reaction (32) has the advantage that highly toxic reagents such as chlorine and phosgene are not used in it. For this reason, CCl₄ has been used in virtually all the subsequent studies involving the carbochlorination of melts.^{145–149}

It has been suggested that CHBr₃, CBr₄,¹⁵⁰ C₂H₅Br, and CH₃I¹⁴² be used for the removal of oxygen-containing impurities from bromide and iodide melts. A significant advantage of carbohalogenation is the fact that this process leads to an appreciable decrease in the concentration of transition metal cations in the melts being purified. However, in the purification of melts by halogen-substituted compounds with a low halogen content, carbon (carbon black) accumulates in the melt and is displaced by the crystallisation front when single crystals are grown.¹⁴³ The presence of a suspension of carbon in alkali metal halide melts is not always desirable and this method cannot therefore be recognised as universal.

The carbohalogenation of the melt leads to the formation of CO₂, which reacts with oxide ions and lowers the equilibrium concentration of O²⁻ and induces the accumulation of the fairly stable carbonate ions CO₃²⁻. The latter are the main form in which oxygen-containing impurities exist in melts purified in this way.

The use of halo-derivatives of silicon for the purification of iodide melts¹⁵¹ is based on the reaction



the product of which is silicon dioxide, which is separated from the melt as a consequence of the differences between the densities. Thermodynamic analysis showed¹⁵² that the effectiveness of the purification of iodide melts diminishes in the sequence SiH₄ > -HI > I₂.

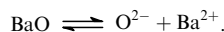
The use of silicon halides for the purification of the melts used in the growing of single crystals does not lead to the appearance of additional impurities, because the processes are carried out in quartz (*i.e.* containing silicon) containers.

Although the methods of purification described are fairly effective in most cases, some kind of oxygen-containing and cationic impurities characteristic of each method always remain in the melt. The method of purification must therefore be selected depending on the aims of the subsequent application of the melt.

3. Dissociation of Lux – Flood bases

The problems of the dissociation of oxide ion donors (Lux – Flood bases) in ionic melts is important both for experimental studies of oxo-acidity and for technological purposes.

Investigators have paid particular attention to strong bases: hydroxide, carbonate, and peroxide ions and barium oxide. The dissociation of the last two bases proceeds in accordance with the equations

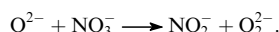


The dissociation of barium oxide (see Section III) leads to the accumulation of ‘foreign ions’ Ba²⁺ in the melt. Furthermore, BaO exhibits a limited solubility in ionic melts. This imposes a series of limitations on the practical use of this compound. It should not be used for the investigation of the solubility of alkaline earth metal oxides with which BaO forms solid solutions, for the investigation of acid–base equilibria in solutions of anions in which Ba²⁺ forms insoluble compounds [Ba₃(PO₄)₂, BaCrO₄, *etc.*], and for the investigation of bromide and iodide melts, in which incomplete dissociation takes place.

As regards the remaining three bases mentioned above, their behaviour in ionic melts requires separate consideration. The point is that alkali metal hydroxides distill without decomposition at temperatures above 1300 °C, while sodium and potassium carbonates melt without decomposition at 854 and 890 °C respectively and the CO₂ pressure over their melts is low even at 1000 °C. The thermal dissociation of sodium peroxides begins at 460 °C, whilst K₂O₂ melts without decomposition at 490 °C.⁵¹ Thus the above bases should be sufficiently stable under the conditions of the majority of investigations (200–800 °C).

On the other hand, their dissolution in melts in the absence of conjugate acid gases (H₂O, CO₂, O₂) in an inert atmosphere should lead, according to the Le Chatelier rule, to complete dissociation with formation of O²⁻, which is bound by the melt cations. The degree of decomposition of the base is determined by the concentration and acidity of the cations, the association of the melt ions, temperature, the solubility in the melt of the conjugate acid gas, and its content in the form of impurities in the inert atmosphere. Owing to the diversity and complexity of these factors, the estimation of the strength of the bases from the results of thermodynamic calculations is frequently incorrect. It is therefore difficult to overestimate the contribution of experimental studies to the solution of this problem.

Potentiometric studies of the dissociation of O₂²⁻ in nitrate melts have shown^{153–156} that at temperatures in the range 200–350 °C the main form in which oxygen ions exist in basic media is O₂²⁻, because oxide ions are oxidised in accordance with the reaction



Naturally, the use of a gaseous oxygen electrode in potentiometric studies leads to the appearance in the atmosphere above the melt of gaseous oxygen, which also oxidises the O²⁻ ions. The decrease in the basicity of the melt both owing to the enhancement of the acid properties of the cations constituting the melt¹⁵⁶ and as a result of the decrease in the concentration of oxygen ions^{157, 158} lowers the stability of O₂²⁻. Under these conditions, the main form in which oxygen anions exist in the melt becomes O²⁻.

Studies of the stability of the O₂²⁻ ions in higher-temperature chloride and sulfate melts^{69, 117, 118, 159} have shown that the peroxide ions may be formed in appreciable amounts only in the presence of gaseous oxygen, whilst in an inert atmosphere they are decomposed fully to O²⁻. The constants of equilibrium (35) at 1100 K in NaCl and Na₂SO₄ melts are 0.05–0.07 and 0.03–0.05 respectively.

The behaviour of carbonate ions in nitrate melts has been investigated.^{160, 161} The experimental results show that CO₃²⁻ dissociates fully in these melts and the oxide ions formed are stabilised as a result of the formation of pyronitrate. On the other hand, it has been shown¹⁶² on the basis of potentiometric studies that carbonate ions are not fully dissociated in fused nitrates. In order to establish the truth, cooled specimens of carbonate solutions in nitrate melts were subjected to titrimetric analysis¹⁶³ by standard methods.¹⁶⁴ It was found that the consumption of the acid on each of the two titration steps is the same and carbonate ions are therefore fully stable in nitrate melts.

The temperature dependence of the dissociation constant for the carbonate ion in KCl–NaCl melts is given by the following equation:¹⁶⁵

$$pK_{\text{CO}_3^{2-}} = 1.32 \times 10^4 T^{-1} - 8.4.$$

At 1000 K, $pK = 4.8$. According to Combes *et al.*,¹⁶⁵ the carbonate ion can be used as the reference base at temperatures above 1000 K, because it should be fully dissociated at low partial pressures of CO_2 .

The use of sodium carbonate as a strong base and in the determination of the solubility products of CaO and MgO in the BaCl_2 – CaCl_2 –NaCl eutectic melt at 600 °C has been described.¹²² The study was performed on the assumption that the base employed is fully dissociated without testing it. The correctness of the results obtained is therefore doubtful.

Potentiometric study of the dissociation of the carbonate ion in the KCl–NaCl melt at 700 °C showed⁶⁶ that the carbonate does not dissociate fully even in the absence of CO_2 in the atmosphere over the melt. The ‘formal’ stability constant of CO_3^{2-} , which was understood as the ratio $[\text{CO}_3^{2-}]/[\text{O}^{2-}]$, was 2.5 ± 0.5 (the concentrations were expressed in mol.%). It was postulated that the partial pressure of CO_2 over the melt is constant. It was found that, even at concentrations of the order of 10^{-3} mol kg^{-1} , the degree of dissociation of CO_3^{2-} in the KCl–LiCl melts at 500 °C and in KCl–NaCl at 700 °C does not exceed 70%.¹³⁰ Thus the hypothesis¹⁶⁵ of the complete dissociation of the carbonate ion at temperatures of ~ 1000 K has not been confirmed.

Only a few quantitative studies on the dissociation of OH^- in melts are known. It has been established potentiometrically^{166, 167} that the constant for equilibrium (9) in the KNO_3 – NaNO_3 melt at 500 K is 10^{-18} . This indicates the stability of OH^- ions. There are no data in the studies quoted on the stability of the hydroxide under a dry atmosphere.

The hydroxide ions do not decompose fully in the KCl–LiCl melt at 400 °C.¹⁶⁸ It may be that this is associated with the fact that the above melt retains water fairly strongly.¹³⁹ According to polarographic^{91, 92} and potentiometric¹³⁰ data, an increase in temperature to 500 °C leads to the complete decomposition of the hydroxide.

In order to investigate equilibrium (9), an O^{2-} donor was added to the KCl–NaCl melt, after which the equilibrium e.m.f.’s were measured at water vapour pressures from 1 to 8 mm Hg.^{101, 169} The calculation of the constant for equilibrium (9), based on the e.m.f.’s obtained, showed that the temperature dependence of the pK in the range 737–817 °C is expressed by the equation

$$pK = 8.15 \times 10^3 T^{-1} - 6.75.$$

It has been shown^{130, 170} that the dissociation of hydroxide ions in alkali metal halides does not correspond to Eqn (9) and that the decomposition of OH^- proceeds in accordance with the scheme



The pK values for reaction (36) in the KCl–LiCl melt at 500 °C and the KCl–NaCl melt at 700 °C are 2.76 ± 0.15 and 2.22 ± 0.06 respectively. In the absence of water vapour in the atmosphere over the melt, equilibrium (36) is fully displaced to the right in both systems. The main form of the existence of hydroxide ions in the melts is dimers, while OH^- ions may be present only in trace amounts and do not exert an appreciable influence on the equilibria investigated. A possible cause of the formation of the dimers $(\text{OH})_2^{2-}$ in the melts is the formation of a hydrogen bond. The existence of such bonds in the OH^- –containing NaCl melt has been indicated.^{102, 171}

Thus, among the bases examined, only Na_2O_2 and NaOH dissociate fully at temperatures above 500 °C and may be recommended for investigation. The application of BaO and CO_3^{2-} is

less desirable, because their solubility is limited and they do not dissociate fully even in high-temperature melts.

V. Conclusion

The above analysis of literature data made it possible to discover a series of causes which prevent the development of studies on oxo-acidity in ionic melts. Evidently the existing view that the properties of ionic and molecular liquids are fundamentally different precludes the application of the approaches and rules developed for molecular solvents to the study and treatment of data on oxo-acidity in ionic melts. This state of affairs led to the isolation of studies on oxo-acidity in melts from the investigation of acid–base equilibria in other media. This resulted not only in a low scientific level of the studies carried out (for example, in nitrate melts) but also in the absence of any qualitative development of the field under consideration. Ultimately, studies on homogeneous equilibria virtually ceased completely and the rate of accumulation of data on the solubilities of oxides diminished sharply.

The results of the investigation of acid–base reactions in nitrate melts require a significant revision. It is essential to alter the very approach to further studies on oxo-acidity: the acid–base solubility products should be determined in oxygen-containing melts, while the acid–base equilibrium constants should be determined in oxygen-free melts, having made sure beforehand that the proposed mechanism of the acid–base process corresponds to reality.

The lack of an explanation of the scatter of data on the solubilities of oxides has still remained the main reason retarding the development of this field of study. Such an explanation has now been given on the basis of the Ostwald–Freundlich equation. In order to establish the general rules governing the solubility of oxides in ionic melts, it has been suggested that a single technique be used for the measurements (the same electrodes, identical initial concentrations of reactants). However, the solubilities obtained should nevertheless be treated with a certain degree of caution because the method of preparation of the initial oxide may exert a fairly considerable influence on them (Fig. 2). Studies on the interaction of melts with gaseous reagents have begun to develop, which may be accounted for by the great applied importance of the results.

Overall, the study of the acid–base interactions in melts is far from being completed. After the boom in the development of this field observed in the 1960s–1970s, which did not, however, yield significant results, the time has come to proceed to serious systematic investigations.

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α -Metalloenylalkylation

V I Boev, L V Snegur, V N Babin, Yu S Nekrasov

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Abstract. Experimental data on α -metallogenylalkylation reactions are generalised and systematised. These reactions are widely used for the synthesis of different metallocene derivatives, many of which may be of practical importance. Advantages and limitations of different variants of these reactions under homogeneous and heterogeneous conditions are discussed, new approaches to their efficient realisation are offered. The bibliography includes 160 references.

I. Introduction

Dicyclopentadienyl complexes of subgroup VIIIA transition metals (metallocenes) as well as their derivatives played an important role in the progress of the chemistry of π -complexes of transition metals.^{1–4} Reactions with the participation of α -metallogenylcarbocations (MCC) the enhanced stability of which is due to the presence of the electron-donating metallocene fragment in the α -position to the cationic centre are of considerable interest.⁵ With the help of these reactions that we have named ' α -metallogenylalkylation', different α -metallogenylalkylated compounds, especially those that could not be synthesised by other methods, may be obtained.^{6,7}

The early stage in the development of this field of chemistry of organometallic compounds (OMC) has been associated with the elaboration of methods of α -ferrocenylalkylation by trialkyl(ferrocenylmethyl)ammonium salts, chloromethylferrocene, and stable salts of α -ferrocenylcarbocations that allowed one to introduce the FcCH_2^+ group into the molecules of different organic and inorganic nucleophilic derivatives.³ Each of these methods, however, has fundamental limitations in the choice of both the ferrocene-containing derivative and the nucleophilic substrate.

† Mc is $\text{C}_5\text{H}_5\text{MC}_5\text{H}_4$, Fc is $\text{C}_5\text{H}_5\text{FcC}_5\text{H}_4$, Rc is $\text{C}_5\text{H}_5\text{RuC}_5\text{H}_4$, and Oc is $\text{C}_5\text{H}_5\text{OsC}_5\text{H}_4$.

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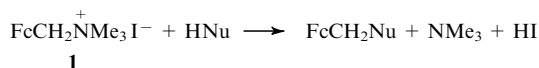
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More suitable and diverse ferrocene-containing reagents in these reactions are α -hydroxyalkylferrocenes which readily generate on treatment with mineral or strong carboxylic acids, the corresponding metallocene cations that react further with nucleophiles. Surprisingly, these ferrocene derivatives have not until recently found extensive application in α -ferrocenylalkylation reactions apart from a few special cases.^{8–11}

Annual reviews on ferrocene by Rockett and Marr that have been published over 20 years (the first review was published in 1972, and the last one was published in 1991) in the *Journal of Organometallic Chemistry* usually quoted 5–10 papers on ferrocenylalkyl compounds.¹² There are separate sections concerning the α -metallogenylalkylation reactions in a monograph³ and Gmelin Handbook¹³ containing extensive experimental data accumulated before 1979, however, there is no specialised review covering this subject. The interest in these studies at present does not decline which is associated with the development of the theoretical aspects of structure and reactivity of MCC¹⁴ as well as with the search for convenient methods for the synthesis of valuable ferrocene-containing compounds.¹⁵ The present report is devoted to the analysis and generalisation of the studies of α -metallogenylalkylation reactions performed during the last 15 years.

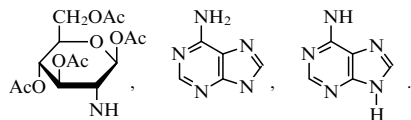
II. α -Ferrocenylalkylation with ferrocenylalkylammonium salts and other onium compounds

Among the reagents for the introduction of the ferrocenylmethyl group in nucleophilic substrates, most attention was paid to quaternary ammonium salts of *N,N*-dimethylaminomethylferrocene^{3,13} which is due to their availability and high reactivity.^{16,17} In particular, new reactions of *N*-, *C*-, *S*-, and *P*-ferrocenylmethylation of different compounds were performed with the help of *N,N,N*-trimethyl(ferrocenylmethyl)ammonium iodide (**1**).^{18–23} In the presence of alkali or sodium carbonate in all the cases elimination of trimethylamine and the corresponding salt of the hydriodic acid occurs.^{18–20} Thus, new ferrocenylalkyl derivatives of nitrogen bases were synthesised:



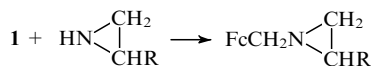
Nu = NHNH₂, NHNHPh, NHC(O)NH₂, NHC(S)NH₂,

NHNHC(O)NH₂, NHNHC(S)NH₂, NHNHC(S)NPh,



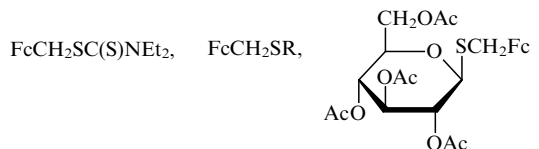
An 8–10-fold excess of hydrazine hydrate is necessary for the preparation of ferrocenylmethylhydrazine,¹⁸ as the action of a 4-fold excess of the nucleophilic agent on the salt **1** gives the product of complete ferrocenylmethylation of hydrazine, tetrakis(ferrocenylmethyl)hydrazine, with a yield of higher than 80%. Condensation of the salt **1** with AcNHCH(COOEt)₂ in ethanol in the presence of EtONa gives the ethyl ester of *N*-acetyl-3-ferrocenyl- α -alanine, which was separated into enantiomers by column chromatography on solid chiral carriers such as *N*-*tert*-butylamides of L-amino acids.²¹

The condensation of 2-*R*-aziridines with the methiodide **1** in aqueous solution in the presence of potassium carbonate gives 2-*R*-1-(ferrocenylmethyl)aziridines in 70%–75% yields.²⁴

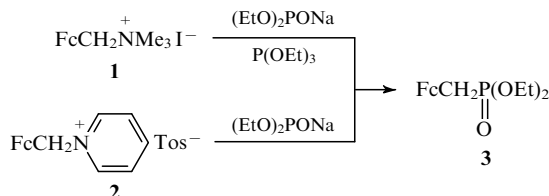


R = H, Me, Et.

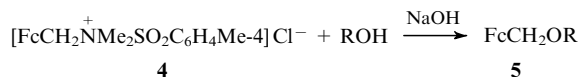
In reactions of the methiodide **1** with sodium diethyldithiocarbamate in aqueous medium,¹⁸ or with thiols (RSH) in the presence of EtONa in ethanol,²² or with 2,3,4,6-tetra-*O*-acetyl-1-thio- β -D-glucopyranose in acetonitrile in the presence of sodium carbonate,¹⁹ the corresponding products of *S*-ferrocenylmethylation are formed in 50%–90% yield:



When a mixture of equimolar amounts of methiodide **1** and sodium diethyl phosphite was refluxed for 17 h in anhydrous xylene, the product of *P*-ferrocenylmethylation, *O,O*-diethyl ferrocenylmethylphosphonate (**3**), was formed in 45% yield.¹⁸ The phosphonate **3** was prepared similarly from ferrocenylmethylpyridinium tosylate (**2**), however, the reaction conditions were milder (refluxing of the reagents for 2 h).¹⁸ The product **3** was also synthesised by the reaction of the salt **1** with triethyl phosphite (the Arbuzov rearrangement) in aqueous medium.¹⁸



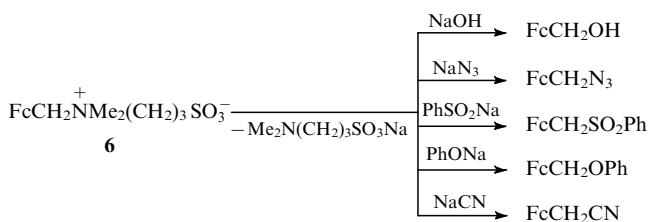
Other salts of *N,N*-dimethylaminomethylferrocene can also enter into the ferrocenylmethylation reaction. Thus, upon reaction of different alcohols with the salt **4** in alkaline medium, *O*-ferrocenylmethylation occurs to give ethers **5** in 75%–92% yield.²⁵



R = Et, Bu, C₈H₁₇, CH₂CH=CH₂, CH₂CH₂OCH₂Fc.

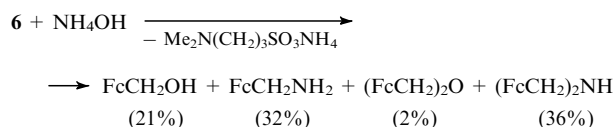
It has been found²⁶ that the ferrocenylmethylation of alcohols by the salts of *N,N*-dimethylaminomethylferrocene does not require the isolation of the ammonium salts in the pure state; it is quite sufficient to add the salt-forming reagent such as dichloroethane or *p*-toluenesulfonylchloride to the mixture of ferrocenylmethylamine, the corresponding alcohol, and alkali. This does not result in a decrease in the yields of the ethers **5**.

The betaine, dimethyl-3-sulfopropyl(ferrocenylmethyl)-ammonium (**6**), is yet another rather efficient ferrocenylalkylating reagent.²⁷ This compound reacts readily with different nucleophilic reagents in aqueous medium to form the products of *O*-, *N*-, *S*-, and *C*-ferrocenylmethylation in 92%–97% yield.²⁷



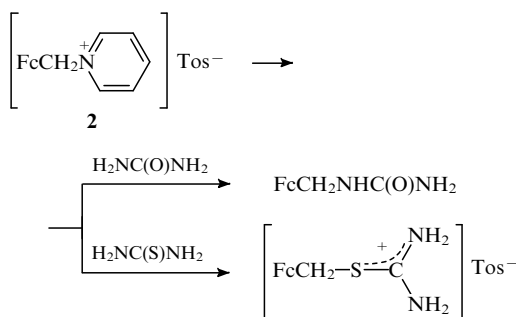
As is evident from the scheme, the second reaction product is sodium *N,N*-dimethylaminopropyl-3-sulfonate, which can be readily separated from the ferrocenylmethyl derivatives due to its high solubility in water.

The activity of the betaine **6** is 10 times higher than that of the salt **1**, which allowed one to perform with its help direct ferrocenylmethylation of ammonia in aqueous solution.²⁷ This resulted in a mixture of products of *N*- and *O*-ferrocenylmethylation, which could be separated by chromatography on alumina.

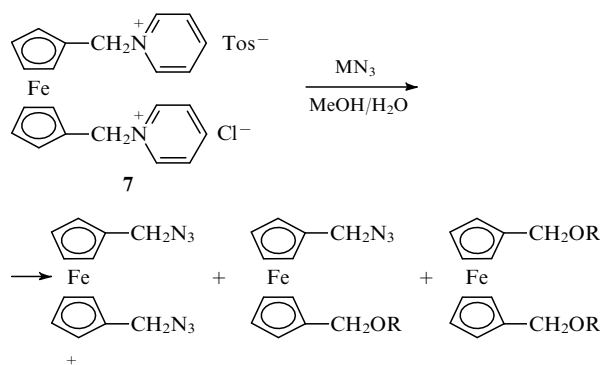


The salts **1** and **2** under analogous conditions practically do not react with aqueous ammonia.²⁷

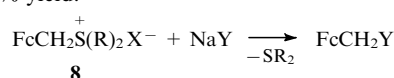
The pyridinium derivatives may be successfully used as the ferrocenylalkylation agents. In particular, the interaction of ferrocenylmethylpyridinium tosylate (**2**) with carbamide in methanol results in the formation of ferrocenylmethylcarbamide, while thiocarbamide under the same conditions formed only *S*-ferrocenylmethylthiuronium tosylate.²³



The reactions of the salt **7** with the salts of hydrazoic acid MN₃ in aqueous methanol gives a mixture of the products of *N*- and *O*-ferrocenylalkylation.²³

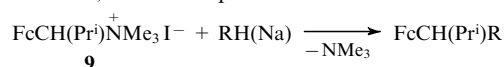


Not only ammonium (compounds **1**, **2**, **4**, and **6**), but also sulfonium salts **8** proved to be rather efficient ferrocenylmethylation reagents.²⁸ In reactions with sodium cyanide and azide, they gave the corresponding ferrocenylmethylation products in 90% to 95% yield.²⁸



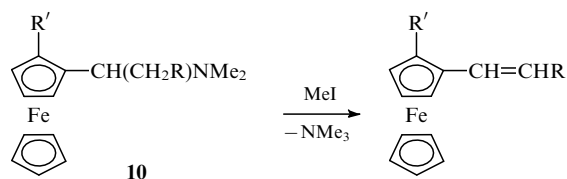
R = Me, Et, CH₂Ph; X = BF₄, ClO₄; Y = CN, N₃.

It is noteworthy that most of the salts, homologues of *N,N*-dimethylaminomethylferrocene of the FcCH(R)N⁺Me₃X[−] (R = Alk) type, are thermally unstable and not easily accessible compounds.^{29,30} Therefore, they did not find extensive application as ferrocenylalkylating reagents. Only the use of the methyl iodide **9** in reactions of α -ferrocenylalkylation of sodium azide and thioctic acid, has been reported.³¹



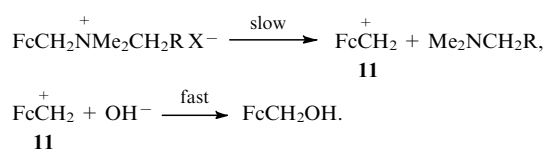
R = N₃, SCH₂COOH.

The salts of *N,N*-dimethylaminoethylferrocene also turned out to be unstable and could not be isolated in the pure state. For instance, the interaction of amines **10** with MeI in acetone results in the formation of the corresponding substituted vinylferrocenes rather than ammonium salts.^{32,33}



R = H, Ph; R' = Alk, PPh₂, SiMe₃.

The study of the reactivity of different trialkyl(ferrocenylmethyl)ammonium salts in reactions with water in alkaline, neutral, and acidic media has revealed¹⁷ that hydrolysis follows the S_N1 mechanism with the intermediate formation of ferrocenylmethyl cation **11** at the rate-determining stage.



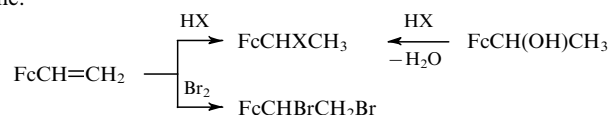
The kinetic isotope effect of the solvolysis of ferrocenyl-1,1-dideuteromethyltrimethylammonium iodide in aqueous medium is not more than 10% at 80 °C ($K_{\text{H}}/K_{\text{D}} = 1.06 \pm 0.04$), while the activation parameters of the reaction at 70–90 °C are close to those for the salt **1** ($\Delta H^\ddagger = 132.6 \pm 3.8$ kJ mol^{−1}, $\Delta S^\ddagger = 54.0 \pm 2.1$ kJ mol^{−1}). These data led to the conclusion³⁴ that in the transition state the α -carbon atom in the carbocation **11** is

bound both with the carbon atom of the five-membered ring of the ferrocene system and with the iron atom; a transition state of the fulvene type is not realised.

Thus, the method of α -ferrocenylalkylation by ferrocenylammonium salts is widely used for the synthesis of numerous derivatives of the ferrocene series, however, it cannot be considered general, as only ferrocenylmethyl compounds may be thus obtained with high yields.

III. Reactions of α -haloalkyl derivatives of ferrocene with nucleophiles

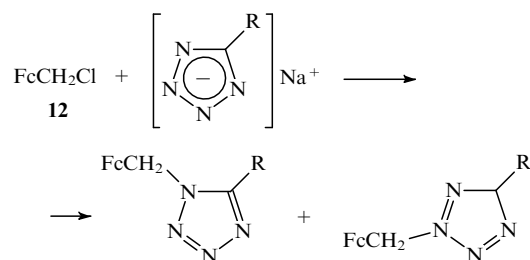
α -Halogen-containing derivatives of ferrocene are unstable at room temperature, they cannot be isolated in the pure state. Tidwell and Traylor³⁵ described the preparation of chloromethylferrocene (**12**) which involved bubbling of HCl through an ethereal solution of ferrocenylmethanol (**13**) in the presence of anhydrous calcium chloride, however neither the isolation procedure nor the constants of the isolated product were reported. When anhydrous hydrogen halides passed either through the solution of vinylferrocene in pentane or through the solution of α -hydroxyethylferrocene in diethyl ether in the presence of Al₂O₃ at −78 °C, α -chloro- and α -bromoethylferrocenes were obtained, and the reaction of bromine with vinylferrocene under the same conditions resulted in the formation of α,β -dibromoethylferrocene.³⁶



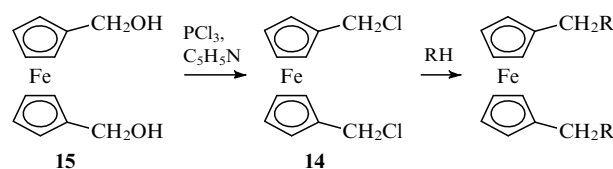
X = Cl, Br.

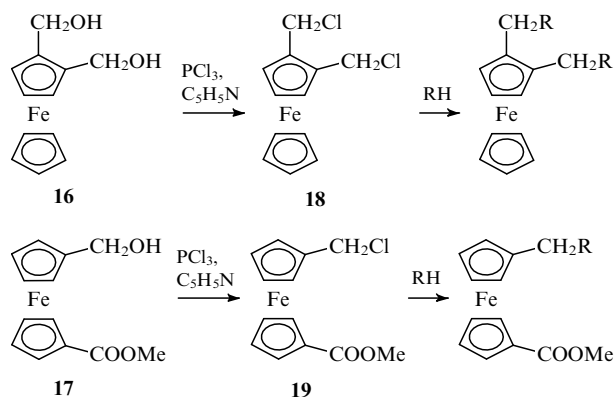
However, all the isolated compounds are extremely unstable and can be stored for several days at low temperature *in vacuo*; they readily undergo hydrolysis in the presence of moisture.³⁶

Chloromethyl- and 1,1'-bis(chloromethyl)ferrocene (**14**) are also formed in the reaction of PCl₃ with the corresponding hydroxyl derivatives of ferrocene **13** and **15** in anhydrous acetone in the presence of pyridine at 0 °C.^{37,38} However, due to their instability, they were used in the α -ferrocenylmethylation reactions of such nucleophilic compounds as sodium azide,²³ carbamide,³⁹ sodium salts of 1,2,4-triazoles^{37,38} and tetrazoles without preliminary isolation. In the latter case, a mixture of 1- and 2-isomers was formed.^{37,38}



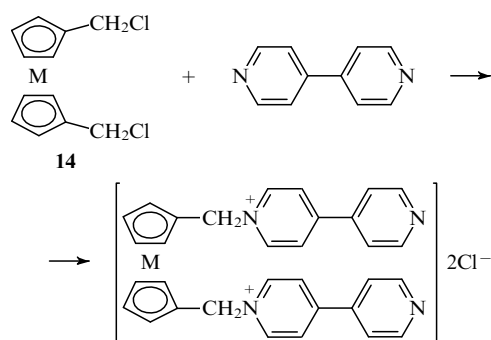
The reactions of ferrocene α -hydroxymethyl derivatives **15**–**17** with PCl₃ in the presence of pyridine in anhydrous THF are reported.^{40,41} The chloromethyl derivatives thus formed **14**, **18**, **19** were used without isolation in the α -ferrocenylalkylation reactions of different nucleophilic substrates such as formamidomalonate, phenol, thiophenol, *N*-methylaniline, and acetylacetone.





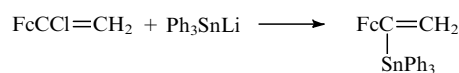
R = C(NHCHO)(COOEt)₂, OPh, SPh, N(Me)Ph, CH(COMe)₂.

In the reactions of dichlorides **14** with 4,4'-bipyridine in DMF, the corresponding pyridinium salts were synthesised with yields of 80% and 39%.⁴²



M = Fe, Ru.

The reaction of relatively stable α -chlorovinylferrocene with lithium triphenylstannane in a mixture of anhydrous THF and diethyl ether results in the formation of 1-ferrocenyl-1-triphenylstannylethylene in 72% yield.⁴³



α -Ferrocenylalkylation by haloalkyl derivatives of ferrocene did not find extensive application because of the low stability of α -haloalkylferrocenes.

IV. Application of α -hydroxyalkyl- and α -alkenylmetallocene derivatives in α -metallocenylalkylation reactions

The synthetic potentialities of α -metallocenylalkylation of nucleophilic derivatives are primarily determined by the availability of the corresponding organometallic component. α -Hydroxyalkylmetallocenes of the VIIIA subgroup are the most convenient and promising alkylation reagents. They are synthetically accessible and demonstrate high stability at room temperature, while under certain conditions the hydroxy group can easily undergo nucleophilic substitution. α -Alkenyl derivatives of metallocenes have also found application as alkylating reagents. Metallocenylalkylation by α -hydroxyalkylmetallocenes can be subdivided into O-, S-, C-, N-, P- and other types of α -metallocenylalkylation depending on the element that forms a new bond as a result of the substitution of the hydroxy group.

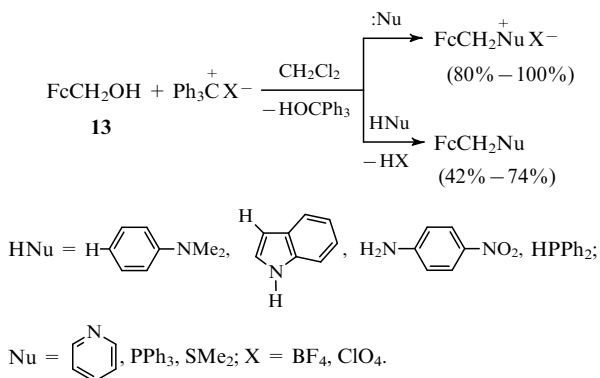
At present, a few methods for the preparation of α -hydroxyalkylmetallocenes are known.^{1-3,7,44-71} Although their consideration is beyond the scope of the present review, the stereoselective reduction of metallocenylketones by lithium aluminium hydride in the presence of optically active com-

pounds⁴⁸⁻⁵⁰ is however worth mention. The enantiomeric metallocenyl-containing alcohols thus prepared on dissolution in acid, form optically active metallocenylcarbocations⁴⁹ that may be used for the synthesis of chiral derivatives of subgroup VIIIA metallocenes by α -metallocenylalkylation. A method of preparation of chiral ferrocenyl alcohols, which allows one to synthesise FcCH(OH)R with an optical purity of higher than 95% and the yields of 80%–89%, deserves special attention.⁷²

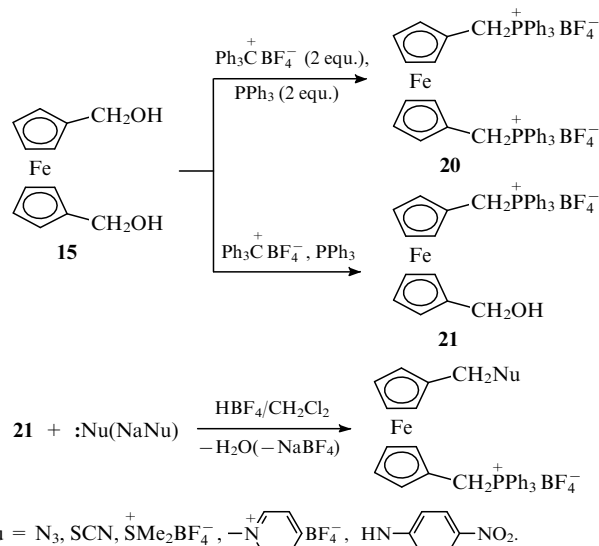
Two methodologies of α -metallocenylalkylation^{3,6,7} by alcohols and alkenes, namely, reactions in homogeneous (HS) and two-phase (TS) systems, may be distinguished.

1. Reactions in homogeneous systems

A general method for α -ferrocenylalkylation in a homogeneous system involves the action of triphenylcarbenium salts at room temperature on an equimolar mixture of α -hydroxyalkylferrocene derivative and a nucleophile in a polar solvent, (anhydrous dichloromethane).^{6,73,74} This method proved especially useful for the synthesis of different onium salts, as they may be easily separated from triphenylmethanol, which is a nonpolar side product of the reaction.^{73,74} In the case of non-ionic α -ferrocenylalkyl compounds chromatographic separation of the reaction products is necessary.⁶



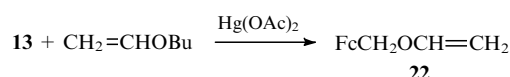
In the reaction of the diol **15** with triphenylphosphine under identical conditions different reaction products are formed depending on the reagent ratio.⁶ The bistrisphenylphosphonium salt **20** was obtained in quantitative yield when the ratio of **15**, triphenylphosphine, and triphenylcarbenium tetrafluoroborate was 1 : 2 : 2, while the monotriphenylphosphonium salt **21** was formed in 62% yield when the reagent ratio is 1:1:1.^{6,73} Due to the presence of the hydroxymethyl group, the latter was successfully used in the synthesis of heteroannular disubstituted ferrocene derivatives in a two-phase liquid–liquid system (see Section VI).



In contrast to ferrocenemethanols **13** and **15**, α -hydroxyalkyl derivatives of ruthenocene and osmocene do not react with nucleophilic reagents under the action of triphenylcarbenium salts under the same conditions.⁶ In this case, only the known products of nucleophilic substitution of the triphenylmethyl series are formed.

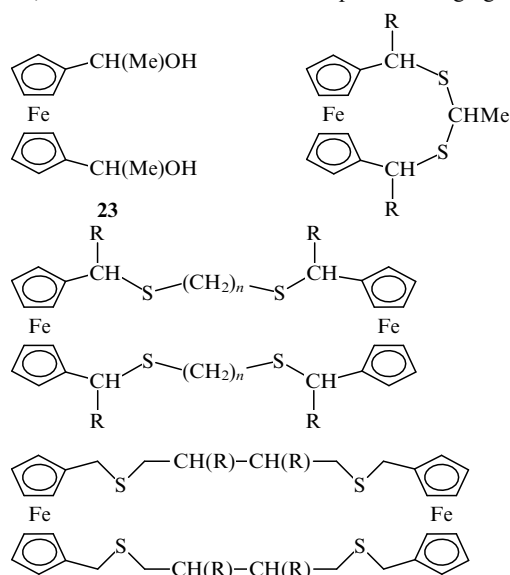
a. O-Alkylation

Numerous examples of α -ferrocenylalkylation of alcohols and phenols at the oxygen atom by α -hydroxyalkylferrocenes are known.³ These reactions readily proceed in the presence of catalytic amounts of organic (acetic, trifluoroacetic) or Lewis acids in an organic solvent (alcohols, CH_2Cl_2). For instance, re-esterification of butyl vinyl ether by ferrocenemethanol **13** in the presence of mercuric acetate gives ferrocenylmethyl vinyl ether **22**, which readily polymerises under the action of cationic catalysts.⁷⁵



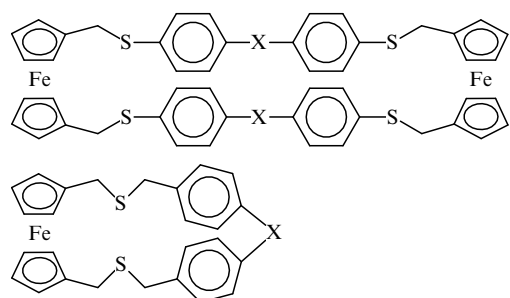
b. S-Alkylation

The reactions of α -hydroxyalkylferrocenes with sulfur-containing nucleophilic reagents have been studied rather thoroughly. For instance, the interaction of the diol **15** or 1,1'-bis(α -hydroxyethyl)ferrocene **23** with dithiols $\text{HSCH}(\text{R})\text{CH}(\text{R})\text{SH}$ or $\text{HS}(\text{CH}_2)_n\text{SH}$ in CH_2Cl_2 in the presence of trifluoroacetic acid leads to the formation of ferrocenophanes with the bridging sulfur atoms,⁷⁶ which are of interest as complex forming ligands.



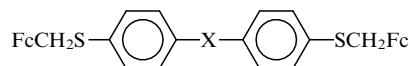
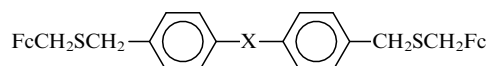
R = H, Me, Ph; $n = 2, 3$.

The analogous reactions of the diol **15** with mercapto derivatives $(4\text{-RC}_6\text{H}_4)_2\text{X}$, where R = SH, CH_2SH , and X = CH_2 , O under similar conditions give the corresponding paracyclophanes.⁷⁷

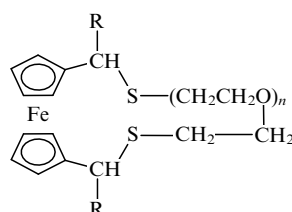


X = CH_2 , O.

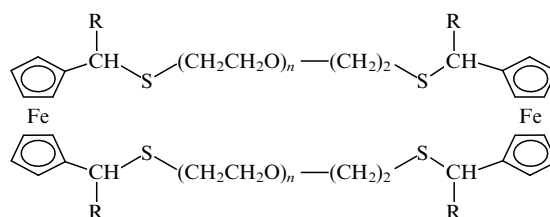
In reactions of the alcohol **13** with the same mercapto derivatives at a reagent ratio of 2:1, linear products of S-ferrocenylmethylation are formed.⁷⁷



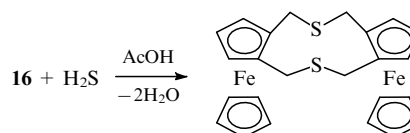
The interaction of the diols **15**, and **23** with bis-mercaptoethers $\text{HS}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2\text{SH}$ ($n = 2, 3$) in a mixture of benzene and CH_2Cl_2 in the presence of CF_3COOH under high-dilution conditions, results in mononuclear ferrocenophanes in high yields.^{78, 79}



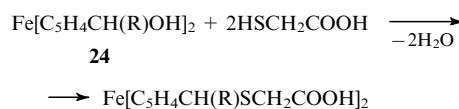
In solutions with higher concentrations the binuclear products may also be obtained; however, their yields are low (5%–7%).⁷⁹



A binuclear ferrocenophane was synthesised in 87% yield by reaction of the homoannular diol **16** with H_2S in acetic acid.⁸⁰

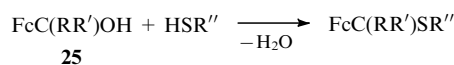


1,1'-Bis[(α -carboxymethylthio)alkyl]ferrocenes were synthesised in 75%–90% yields in reactions of heteroannular ferrocenyldiols **24** with thioglycolic acid in CH_2Cl_2 in the presence of CF_3COOH . They are formed as a mixture of stereoisomers that could not be separated into enantiomers by TLC.⁸¹



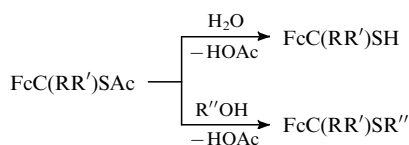
R = Me, Et, Prⁱ.

The reaction of the α -hydroxyferrocenyl derivatives **25** with thiophenol,⁸² $\text{HSCH}_2\text{CH}(\text{OH})\text{CH}_2(\text{OH})$ ⁸³ and thioacetic acid⁸⁴ under the same conditions results in a high yield of the corresponding products of S- α -ferrocenylalkylation.



R = H, R' = H, Me, Et, Prⁱ, Ph; R = Me, R' = Me, Ph;
R'' = SPh, $\text{CH}_2\text{CH}(\text{OH})\text{CH}_2(\text{OH})$, Ac.

The resulting thioacetates $\text{FcC}(\text{RR}')\text{SAc}$ readily undergo hydrolysis and alcoholysis, which allows one to obtain the corresponding thiols and thioethers in high yields.⁸⁴

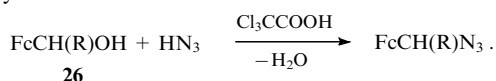


R'' = Me, Et.

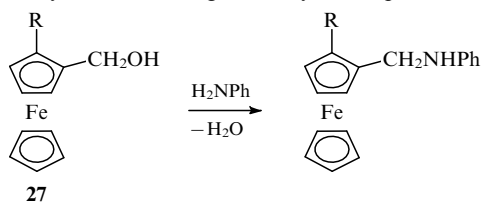
The study of the kinetics of S- α -ferrocenylalkylation of thioglycolic acid under the action of FcCH(Me)OH in CH₂Cl₂ in the presence of CF₃COOH demonstrated that the process has an activation energy of 83.04 kJ mol⁻¹ (see Ref. 85); it is completed in 20 min at 20 °C and results in the formation of the acid FcCH(Me)SCH₂COOH. The authors discovered the intermediate formation of vinylferrocene FcCH=CH₂. Its quantity is minimised in the temperature range of 20–30 °C.

c. N-Alkylation

The synthesis of ferrocenylalkylazide in the reaction of hydrazoic acid with the alcohol **26** (R = Ph) in benzene in the presence of trichloroacetic acid is one of the first examples of N- α -ferrocenylalkylation.⁸⁶

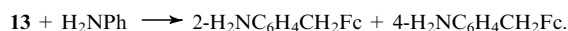


Later, this reaction was extended to a wide range of nitrogen-containing nucleophiles.⁸⁷ Thus the interaction of aniline with alcohols **27** in aqueous medium gives products of N-ferrocenylalkylation in poor yields.^{87,88} Benzylamine and piperidine⁸⁸ under these conditions proved to be non-reactive, which is evidently due to their high basicity in comparison with aniline.



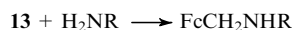
R = H, I, CH₂NHPh.

Heating of equimolar amounts of ferrocenemethanolcarbinol **13** with aniline in AcOH at 130 °C leads to the products of C-ferrocenylmethylation at the aromatic nucleus, which is explained by the possibility of migration of the ferrocenylmethyl group from the nitrogen atom towards the aromatic nucleus at high temperature.⁸⁹

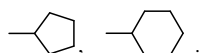


Indeed, heating of N-ferrocenylmethylaniline up to 130 °C results in rearrangement with the formation of the above-mentioned products of C-alkylation with the ratio of *ortho*- and *para*-isomers 1.6:1. However, if the ratio of the starting reagents, the alcohol **13** and aniline, is 2:1, only the products of di- and mono-N-ferrocenylmethylation, PhN(CH₂Fc)₂ and PhNHCH₂Fc, are formed under the same conditions.⁸⁹

The study of the effect of the acidity of the medium on the reaction of the alcohol **13** with different amines has demonstrated that in the case of aliphatic amines the highest yields (up to 97%) are achieved in acetic acid at pH = 5.2–4.9, while in the case of aromatic amines yields of 70%–95% are achieved in aqueous methanol at pH = 7.9–9.7.^{10,90}

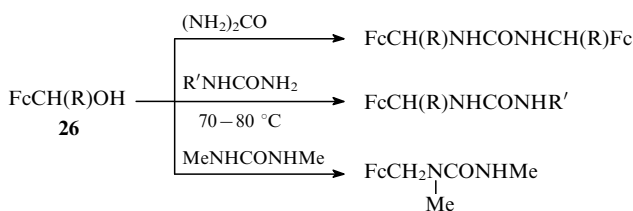


R = Bu^t, CH₂Ph, Ph, 4-NO₂C₆H₄, 2,4-(NO₂)₂C₆H₃, C(O)NH₂,



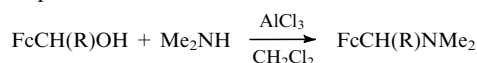
N- α -Ferrocenylalkylation of urea and its derivatives is also performed in high yields (70%–90%) by alcohols **26** in acetic

acid. Usually, alkylation proceeds at the unsubstituted amino-group, however in the case of N,N'-dimethylurea the product of substitution at the N-methylaminogroup has also been isolated. An excess of alcohols **26** results in the formation of the products of the double N,N'-di- α -ferrocenylalkylation in low yields.⁹¹



R = H, Me, Ph; R' = Me, Ph.

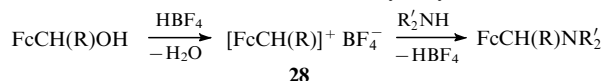
A method for the conversion of α -hydroxyalkylferrocenes into amines^{92–94} by substitution of the hydroxyl group under the action of dimethylamine or tetramethyldiaminomethane in the presence of acetic acid or Me₂NH·AlCl₃ in CH₂Cl₂ has been developed.



R = H, Me, Et.

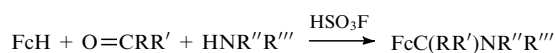
However, the amines formed (R = Me, Et) undergo the Hoffmann degradation on heating in AcOH with the formation of α -substituted vinylferrocenes, which readily polymerise under the reaction conditions.⁹²

Another method for the preparation of α -ferrocenylalkylamines^{95,96} is based on the generation of the corresponding α -ferrocenylcarbocations from α -ferrocenylalkanols in strong acids and their further reaction with amines. It is sometimes possible to isolate the carbenium salts. Thus, the alcohols **26** (R = Me, Ph) under the action of HBF₄ in a mixture of diethyl ether and acetic anhydride are converted into carbenium salts **28**, which have been isolated in the pure state.⁹⁵ They readily react with amines in CH₂Cl₂ to form α -ferrocenylalkylamines.^{95,96}



R = Me, Ph; R' = Me, Et.

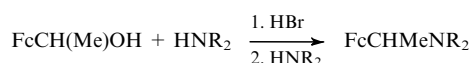
Hermann and Ugi^{66,70} synthesised a large series of α -ferrocenylalkylamines by a 'three component' reaction of ferrocene with a carbonyl compound and an amine in a mixture of CCl₃COOH and AcOH in the presence of fluorosulfonic acid.



R, R' = H, Alk, Ph; R'', R''' = H, Alk.

Taking into account the availability of the initial reagents, this reaction may be considered as a simple preparative method for the synthesis of α -ferrocenylalkylamines despite the low yields. Ugi *et al.*⁹⁷ extended this method for the preparation of chiral α -ferrocenylalkylamines which were used for the stereospecific synthesis of peptides.

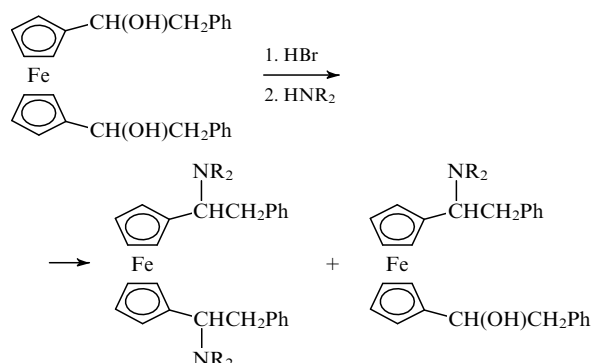
Successive interaction of α -hydroxyethylferrocene with gaseous HBr in benzene and then with amines results in the corresponding α -aminoethylferrocenes which were synthesised in 60%–85% yields.⁹⁸



R = Me, Prⁱ,

Reactions with ammonia lead to a mixture of mono-, bis-, and tris- α -ferrocenylethylamines.⁹⁸

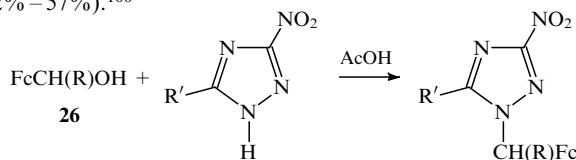
The reaction of 1,1'-bis(α -hydroxy- β -phenylethyl)ferrocene with the excess of R_2NH under analogous conditions results in a mixture of products, viz., 1,1'-bis(α -amino- β -phenylethyl)ferrocenes (yield 50%–70%) and 1-(α -hydroxy- β -phenylethyl)-1'-(α -amino- β -phenylethyl)ferrocenes (yield 15%–30%).⁹⁹



$R = \text{Me, Et.}$

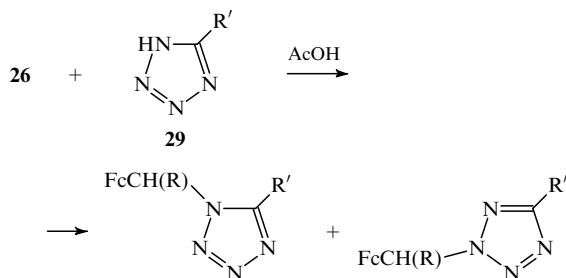
It is interesting to note that the reaction of 1,1'-bis(α -hydroxyethyl)ferrocene **23** with HBr and then with dimethylamine leads to a more complicated mixture of products, which contains 1,1'-bis(α -dimethylaminoethyl)ferrocene, 1-(α -dimethylaminoethyl)-1'-vinylferrocene, and 1,1'-divinylferrocene in the yields of 35%, 45%, and 15% respectively.⁹⁹ Butler *et al.*^{98,99} suggest that under the specified conditions the alcohols are first converted into α -bromo-, or α,α' -dibromoalkylferrocenes, and then nucleophilic substitution of bromine by the amino group occurs.

Besides amines, the nitrogen-containing heterocyclic compounds, such as 1,2,4-triazole¹⁰⁰ and tetrazole^{100–102} derivatives also readily enter into the reaction of N- α -ferrocenylalkylation. The interaction of the alcohols **26** with 3-nitro- and 3,5-dinitro-1,2,4-triazoles in AcOH results in the formation of the corresponding 1-substituted triazoles whose yields vary considerably (12%–57%).¹⁰⁰



$R = \text{H, Me, Ph; } R' = \text{H, NO}_2.$

The products of the reactions of the alcohols **26** with the substituted triazoles **29** are mixtures of isomeric 1- and 2- α -ferrocenylalkyltetrazoles,¹⁰⁰ the ratio thereof depending on the nature of both the substituent R' in the heterocycle and on the substituent R in the alcohols. In particular, increase in the size of the substituent R results in a decrease in the yield of the 1-isomer.



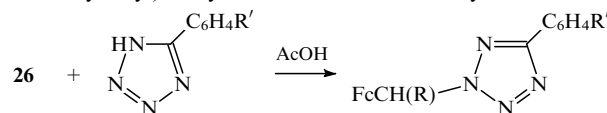
$R' = \text{H, Me, NO}_2.$

The following results were obtained in the alkylation of the derivatives of tetrazole **29** and 1,2,4-triazole by the diols **15**, and **23** in AcOH.¹⁰⁰ A mixture of all three possible isomers (1,1'-, 2,2'-, 1,2'-) is formed from tetrazole; 5-methyltetrazole gives two isomers (2,2'- and 1,2'-), while only the 2,2'-substituted isomer is obtained from 5-nitrotetrazole. In the reaction of 3-nitro- and 3,5-

dinitro-1,2,4-triazoles only 1,1'-disubstituted products of α -ferrocenylalkylation have been isolated.

The detailed study of the alkylation of tetrazole by α -hydroxyethylferrocene in carboxylic acids¹⁰¹ has demonstrated that in CF_3COOH , 1- and 2-isomers are formed in the ratio of 2.4:1, while in AcOH the ratio between these isomers is close to 1:1. These differences in the isomeric composition are due to the formation of the protonated tetrazole in CF_3COOH , and as a consequence ferrocenylalkylation proceeds *via* a different mechanism.¹⁰¹

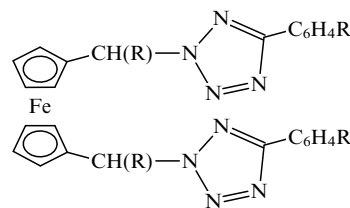
The α -ferrocenylalkylation of 5-aryltetrazoles in AcOH, independent of the structure of alcohols **26** and the electronic properties of the substituents in the heterocyclic nucleus, results only in 2-(α -ferrocenylalkyl)-5-aryltetrazoles in 80%–85% yield.¹⁰²



$R = \text{H, Me, Ph; } R' = \text{H, 3-Me, 4-Me, 4-Br, 4-OMe, 3-NO}_2.$

According to Shirobokov *et al.*,¹⁰² tetrazolate-anions and α -ferrocenylcarbocations are the reactive species in this reaction, and the selectivity of the process is determined by steric factors in the substrate and alkylation agent.

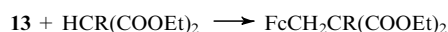
In the alkylation of 5-aryltetrazoles by the diols **15**, and **23** under the same conditions, ferrocene compounds containing two tetrazole rings with the C–N bond in position 2 are formed.¹⁰²



$R = \text{H, Me.}$

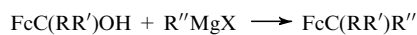
d. C-Alkylation

There are only few examples of the reactions of α -hydroxyalkylferrocenes with CH-acids performed in homogeneous systems.¹⁰³ The CH-acids with activated methylene and methine groups have been most studied. Thus heating of alcohol **13** with the C-substituted diethyl malonates in DMF gave the corresponding ferrocenylmethyl derivatives in 40%–50% yield.¹⁰³



$R = \text{H, Me, Ph.}$

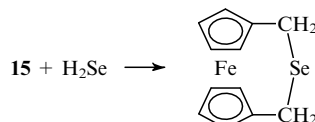
α -Hydroxyalkylferrocenes react with organomagnesium compounds¹⁰⁴ to form a multicomponent mixture. It should be noted that under these conditions neither diphenyl- nor triphenylmethanols react with MeMgI .¹⁰⁴



$R = R' = \text{Me, Ph; } R = \text{H, } R' = \text{CH=CHPh; } R = \text{H, } R' = \text{Ph; } R'' = \text{Me, Et, X = Br, I.}$

e. Se-Alkylation

The interaction of the diol **15** with hydrogen selenide in AcOH in the presence of CF_3COOH , resulting in the formation of 2-seleno-[3]-1,1'-ferrocenophane in 51% yield, has been reported.¹⁰⁵



2. Reactions in two-component systems

Reactions of α -hydroxyalkylmetallocenes with different nucleophilic compounds proceed most efficiently in two-component systems, such as liquid-liquid (system *A*)¹⁰⁶ and liquid-solid (system *B*).^{73, 107} In the former case, the reaction of equimolar amounts of α -hydroxyalkylmetallocenes and nucleophilic substrates is carried out at room temperature with vigorous stirring in a two-phase system consisting of an organic solvent (CH_2Cl_2 , $\text{C}_2\text{H}_4\text{Cl}_2$, CHCl_3 , CCl_4 , or benzene) and aqueous solution (45%–70%) of an acid HX ($\text{X} = \text{BF}_4$, ClO_4 , or I).^{106, 108} Under these conditions reactions proceed predominantly at the organic-inorganic interface: the organic phase contains the hydrophobic metallocene-containing compound (initial and/or reaction product), and the aqueous phase contains acid HX and/or water-soluble reaction products (NaX , KX , BrMgX , etc.). The polar hydroxy group of the organometallic substrate is probably exposed to the aqueous phase and is thus available for protonation, while the metallocene nucleus, on the contrary remains in the organic phase and is not subjected to protonation and oxidation. The procedure of α -ferrocenylalkylation in the system *A*, allows one on the one hand, to attain high acidity at the interface ($H_0 = -7$ to -9),¹⁰⁹ which facilitates the formation under mild conditions of thermodynamically stable MCC,⁵ and, on the other hand, to reduce the possibility of oxidation of the metallocene-containing substrates, which readily occurs in acidic media.¹¹⁰ This is obviously due to the small probability for the contact (except for the interface) of the metallocene-containing component in the organic phase with the acid HX in the aqueous phase. The carbenium reaction centre and the non-polar part of the MCC formed are in different phases. Therefore, the efficient interaction of the carbenium centre with the corresponding nucleophilic reagent may occur, other side reactions (rearrangement, dimerisation, polymerisation, formation of ethers, etc.) which are characteristic of the MCC are practically excluded.^{1–4}

When system *B* is used,^{73, 107, 111} the interaction of the equimolar amounts of α -hydroxyalkylmetallocenes with the nucleophilic reagents occurs under vigorous stirring of an organic solvent (CH_2Cl_2 , $\text{C}_2\text{H}_4\text{Cl}_2$, CHCl_3 , benzene, or xylene) and solid (cation-exchange resins or zeolites in the H-form). In this case, the formation of the corresponding MCC occurs only in the adsorption layer on the surface of the solid phase, they react further with the nucleophilic substrate. As in the case of system *A*, side transformations of MCC are minimal.

The above-mentioned advantages and peculiarities of the α -metallocenylalkylation in the two-phase systems *A* and *B* allow one to extend considerably the range of both metallocenyl and nucleophilic reagents and to increase the yields and purity of the products isolated. Moreover, reactions of organometallic compounds can be thus performed in aqueous-organic media in air rather than in anhydrous solvents and in an inert atmosphere.

For the sake of completeness and for better systematisation of the synthetic data, and convenience of their use, the information of this section is presented largely in the form of tables containing the detailed information concerning the initial compounds and reagents, reaction conditions, yields, and the structure of the products of α -metallocenylalkylation.

a. C- α -Metallocenylalkylation

Weak CH-acids, activated aromatic, organomagnesium and organomercury derivatives, and alkyl derivatives of ferrocene may be used as nucleophilic reagents when reactions are performed in the two-phase systems *A* and *B*. Various α -hydroxymetallocenyl derivatives of the subgroup VIIIA elements were used in these reactions (Table 1), however, their structural peculiarities in most cases only slightly affected the character of the products formed. The choice of the nucleophilic reagents was mostly determined by both their reactivity and the stability of the functional groups of the molecule under the reaction conditions.

In the system *A*, α -hydroxymetallocenyl derivatives (Table 1) react¹⁰⁸ only with CH-acids with pK_a 's in the range of 9–13.¹¹⁷

Compounds with lower mobility of the hydrogen atoms ($pK_a = 16$ –21),¹¹⁷ such as phenylbenzoylmethane, acetophenone, acetone, and fluorene, do not react under these conditions.¹⁰⁸ It is interesting that phenol and α -naphthol react neither in the system *A*, nor *B*.^{108, 112}

The interaction of α -hydroxyalkylmetallocenes with highly nucleophilic aromatic compounds (Table 1) in the systems *A* and *B* occurs¹¹² chemoselectively in accordance with the general features¹¹⁸ of electrophilic substitution. In this case, it is possible to introduce sequentially several similar or different metallocenylalkyl groups into the molecules of nucleophilic compounds.

Under the conditions described, organomercury or organomagnesium compounds may enter into the metallocenylalkylation reaction. The direction of the reaction in this case sometimes greatly depends on the peculiarities of the nucleophile structure. Thus, the reaction of 1-bromomagnesiumindole with the alcohols **13** or $\text{CpRuC}_5\text{H}_4\text{CH(R)OH}$ in the system *A* gives only products of N- α -metallocenylalkylation (Table 2) rather than C-alkylation.¹¹² In the system *A*, the organomagnesium derivatives RMgBr with alkyl radicals ($\text{R} = \text{Me}$, Et , CH_2Ph , $\text{CH}_2\text{CH}=\text{CH}_2$) decompose with the elimination of the corresponding hydrocarbons RH , the decomposition is too fast to allow reactions with alcohols.¹¹² Reactions of these alcohols with organomagnesium compounds, containing aryl radicals or with Iotsich reagents gives the products of decomposition of initial reagents (benzene, naphthalene, phenylacetylene) in 10%–25% yields together with the products of α -metallocenylalkylation (Table 1).¹¹² Also, the reaction of Grignard reagents with the alcohol **13** gives 2%–3% of 1,2-diferrocenylethane, while in the reaction with $\text{CpRuC}_5\text{H}_4\text{CH(Me)OH}$, 3%–5% of polymeric substances are formed.¹¹²

The interaction of α -hydroxyalkylmetallocenes with the organomercury compounds R'HgBr in the system *A* containing different types of protic acids HX , in most cases results in the products of α -metallocenylalkyldemercuration with considerably variable yields (see Table 1).¹¹⁶ In this case, side products are also formed: R'H , polymeric compounds, and mercury-containing metallocenes. Obviously, the formation of R'H occurs as a result of the competitive protodemercuration of the initial mercury-containing derivatives, which in many cases is the main direction of the reaction. It has been found,¹¹⁶ that the activity of the mercury-containing substrates in α -metallocenylalkyldemercuration reactions decreases with the decrease in the electron accepting character of the R' radicals in the series: $\text{CH}_2\text{CHO} > \text{CH}_2\text{C(O)Ph} > \text{CH}_2\text{C(O)Me} > \text{CH}_2\text{COOMe} > \text{Ph} > \text{Alk}$.

The maximum yields of the products of α -metallocenylalkyldemercuration were achieved when 56% HI was used, while the minimum yields were observed with HCl , HClO_4 , and HBF_4 .¹¹⁶ This can probably be explained by the specific role of the iodide ion: because of its high nucleophilicity iodide is readily coordinated by the mercury atom, thus polarising the $\text{C}-\text{Hg}$ bond of the initial complex.¹²⁰ As a result, the reactivity of R'HgBr is enhanced at the final stage of α -metallocenylalkyldemercuration.

Comparison of the yields in bromomercurioacetaldehyde reactions with different α -hydroxyalkylmetallocenes in the two-phase system $\text{CH}_2\text{Cl}_2 - \text{HI}$ testifies¹¹⁶ that their activity changes in the series: $\text{FcCH}_2\text{OH} > [\text{FcCH(Me)OH}; \text{RcCH(Me)OH}] > \text{FcCH(Ph)OH} > \text{OcCH(Ph)OH}$. This regularity is presumably determined by the increase in the steric hindrance of the hydroxy group. The nature of the metal atom in this case practically does not affect the yields of the products of α -ferrocenylalkyldemercuration.¹¹⁶

In contrast to α -hydroxyalkylferrocenes,¹¹⁵ the analogous ruthenocene and osmocene compounds do not give the corresponding derivatives of 1,2-dimetallocenylethane in reactions with powdered copper in system *A*.⁶

In system *A*, it is possible to perform the alkylation of ferrocene and its homologues, sym-octamethyl- and 1,1'-diethylferrocene; the corresponding binuclear diferrocenylalkanes were

Table 1. Reagents, conditions and yields of product of C- α -metallocenylalkylation.

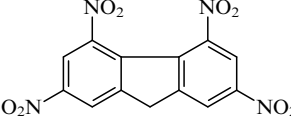
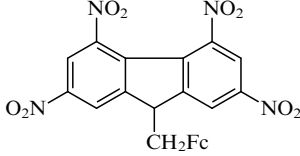
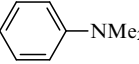
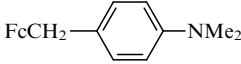
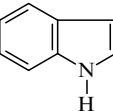
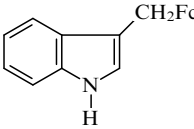
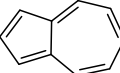
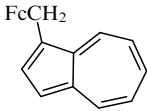
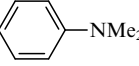
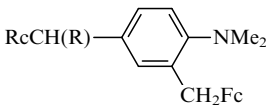
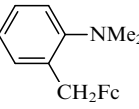
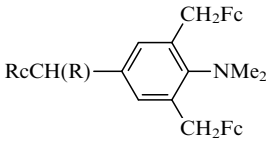
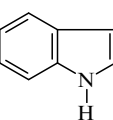
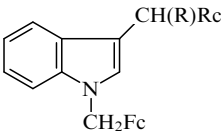
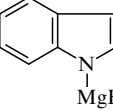
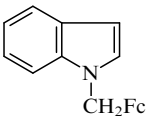
α -Hydroxy-alkylmetal-locene	Nucleophile	Reaction conditions	Reaction time /min	Product	Yield (%)	Ref.
FeCH ₂ OH	H ₂ C(COR) ₂	<i>A</i> (CH ₂ Cl ₂ / HX, X = BF ₄ , ClO ₄)	30 30 120 120 120	FeCH ₂ CH(COR) ₂	100 (R = Me) 100 (R = Ph) 98 (R = C ₆ H ₄ OMe-4) 78 (R = C ₆ H ₃ (OMe) ₂ -2,4) 100 (R = C ₆ H ₂ (OMe) ₃ -3,4,5)	108
		<i>A</i> (CH ₂ Cl ₂ / HBF ₄)	240		100	108
	H ₂ C(COMe) ₂ ^a	<i>A</i> (CH ₂ Cl ₂ / HBF ₄)	120	(FcCH ₂) ₂ C(COMe) ₂	94	108
		<i>A</i> (CH ₂ Cl ₂ / HBF ₄)	160		73	108
		<i>A</i> (CH ₂ Cl ₂ / HBF ₄)	40		95	108
		<i>A</i> (CH ₂ Cl ₂ / HBF ₄)	65		77	73
RcCH(R)- 		<i>A</i> (CH ₂ Cl ₂ / HClO ₄)	60	RcCH(R)- 	58 (R = Me) 53 (R = Ph)	112
RcCH(R)- 		<i>A</i> (CH ₂ Cl ₂ / HClO ₄)	120	RcCH(R)- 	62 (R = Me) 56 (R = Ph)	112
		<i>A</i> (CH ₂ Cl ₂ / HClO ₄)	120		43 (R = Me) 45 (R = Ph)	112
		<i>A</i> (CH ₂ Cl ₂ / HClO ₄)	10		83	112
ArMgBr		<i>A</i> (CH ₂ Cl ₂ / HClO ₄)	5	ArCH ₂ Fc	43 (Ar = Ph) 54 (Ar = 1-Naphthyl)	112
PhC $\equiv$ CMgBr		<i>A</i> (CH ₂ Cl ₂ / HClO ₄)	15	PhC $\equiv$ CCH ₂ Fc	62	112
BrMgC $\equiv$ CMgBr		<i>A</i> (CH ₂ Cl ₂ / HClO ₄)	10	FeCH ₂ C $\equiv$ CCH ₂ Fc	62	112

Table 1 (continued).

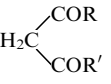
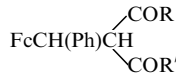
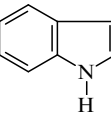
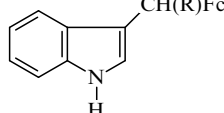
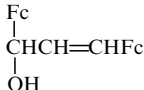
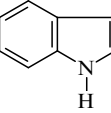
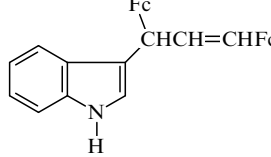
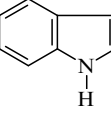
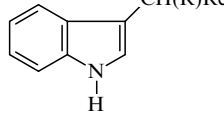
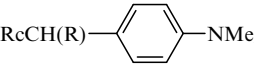
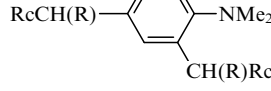
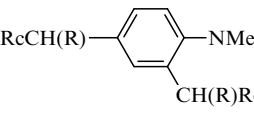
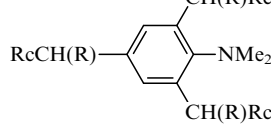
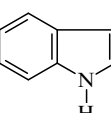
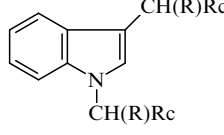
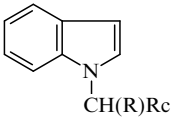
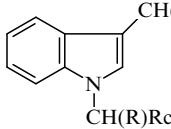
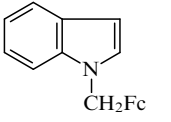
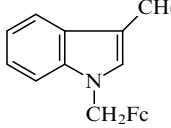
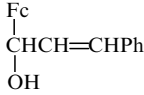
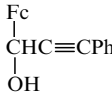
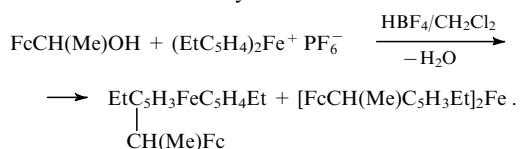
α -Hydroxy-alkylmetal-locene	Nucleophile	Reaction conditions	Reaction time /min	Product	Yield (%)	Ref.
FcCH ₂ OH	HCR(COR') ₂	<i>B</i> (C ₆ H ₆ –Ca ²⁺ –montmorillonite)	120–150	FcCH ₂ CR(COR') ₂	70–80 (R = H, NHCHO; R' = Me, OEt)	111
FcCH(R)OH	H ₂ C(COR') ₂	<i>A</i> (CH ₂ Cl ₂ /HBF ₄)	30 45	FcCH(R)CH(COR') ₂	81 (R = Me, R' = OEt) 85 (R = Ph, R' = Me)	108
FcCH(Ph)OH		<i>B</i> [MeC ₆ H ₅ or C ₆ H ₆ –zeolites NaA (5Å) CaA (3Å)]	3600		56 (R = R' = Me) 65 (R = Me, R' = OEt) 60 (R = R' = OEt)	107 113 113
FcCH(R)OH		<i>B</i> (CH ₂ Cl ₂ /cationite KU-2)	200 180		66 (R = Me) 77 (R = Ph)	73
FcCH(Me)OH	FcH	<i>A</i> (CH ₂ Cl ₂ /HBF ₄)	3	FcCH(Me)Fc	60	114
	(C ₅ H ₄ Et) ₂ Fe	<i>A</i> (CH ₂ Cl ₂ /HBF ₄)	5	[C ₅ H ₃ (FcCHMe)Et]Fe(C ₅ H ₄ Et) [C ₅ H ₃ (FcCHMe)Et] ₂ Fe	54	114
	(C ₅ HMe ₄) ₂ Fe	<i>A</i> (CH ₂ Cl ₂ /HBF ₄)	5	[C ₅ Me ₄ (FcCHMe)]Fe(C ₅ HMe ₄)	50	114
		<i>B</i> (CH ₂ Cl ₂ /cationite KU-2)	92		66	73
RcCH(R)OH	C ₆ H ₅ NMe ₂	<i>A</i> (CH ₂ Cl ₂ /HBF ₄)	60 90	RcCH(R)(C ₆ H ₄ NMe ₂) ₄	72 (R = Me) 68 (R = Ph)	112
		<i>A</i> (CH ₂ Cl ₂ /HBF ₄)	120 150		78 (R = Me) 72 (R = Ph)	112
		<i>A</i> (CH ₂ Cl ₂ /HBF ₄)	120		57 (R = Me) 43 (R = Ph)	112
		<i>A</i> (CH ₂ Cl ₂ /HBF ₄)	150		45 (R = Me) 38 (R = Ph)	112
		<i>A</i> (CH ₂ Cl ₂ /HBF ₄)	150 180		64 (R = Me) 56 (R = Ph)	112

Table 1 (continued).

α -Hydroxy-alkylmetal-locene	Nucleophile	Reaction conditions	Reaction time /min	Product	Yield (%)	Ref.
RcCH(R)OH		A (CH ₂ Cl ₂ /HBF ₄)	150 180		78 (R = Me) 71 (R = Ph)	112
RcCH(Me)OH		A (CH ₂ Cl ₂ /HBF ₄)	120		43	112
	ArMgBr	A (CH ₂ Cl ₂ /HClO ₄)	15	ArCH(Me)Rc	45 (Ar = Ph) 37 (Ar = 1-Naphthyl)	112
RcCH(R)OH	PhC $\equiv$ CMgBr	A (CH ₂ Cl ₂ /HClO ₄)	20	PhC $\equiv$ CCH(R)Rc	61 (R = Me) 46 (R = Ph)	112
RcCH(Me)OH	BrMgC $\equiv$ CMgBr	A (CH ₂ Cl ₂ /HClO ₄)	20	RcCH(Me)C $\equiv$ CCH(Me)Rc	59	112
FcCH(R)OH		A Cu (CH ₂ Cl ₂ /HX, X = BF ₄ , ClO ₄)	120 240	FcCH(R)–CH(R)Fc	72 (R = H) 70 (R = Ph)	115
FcCH ₂ OH		B Cu (CH ₂ Cl ₂ /cationite KU-2)	300	FcCH ₂ CH ₂ Fc	62	73
FcCH(R)OH	R'HgBr	A (CH ₂ Cl ₂ /HI)	120	FcCH(R)R'	6 (R = H, R' = Me) 8 (R = H, R' = Et) 21 (R = Me, R' = Ph) 33 (R = H, R' = CH ₂ Ph) 36 (R = Me, R' = CH ₂ COMe) 62 (R = H, R' = CH ₂ COPh)	116
	RHgBr	A (CH ₂ Cl ₂ /HI)	120	FcCH(R)CH=CHPh	46 (R = CH ₂ CHO) 38 (R = CH ₂ COPh)	116
	RHgBr	A (CH ₂ Cl ₂ /HI)	120	FcCH(R)C $\equiv$ CPh	28 (R = CH ₂ CHO) 26 (R = CH ₂ COPh)	116
RcCH(R)OH	R'HgBr	A (CH ₂ Cl ₂ /HI)	120	RcCH(R)R'	45 (R = Me, R' = CH ₂ CHO) 38 (R = Ph, R' = CH ₂ CHO) 38 (R = Me, R' = CH ₂ COMe) 42 (R = Ph, R' = CH ₂ COPh)	116
OcCH(R)OH	R'HgBr	A (CH ₂ Cl ₂ /HI)	120	OcCH(R)R'	34 (R = Me, R' = CH ₂ CHO) 33 (R = Ph, R' = CH ₂ COMe)	116

^a Reagent ratio is 2 : 1.

thus formed in high yields.¹¹⁴ In this system, the 1,1'-diethylferrocenium salt can also be alkylated:⁷



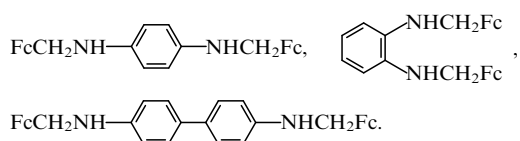
It is difficult to interpret this result without additional data, however, it may be suggested that this process occurs as a result of reduction of the ferrocenium cation and further alkylation of diethylferrocene formed according to the usual scheme. Another possible interpretation of this reaction may be intramolecular electron transfer in the methylferrocenylcarbenium cation followed by free radical substitution in the 1,1'-diethylferrocenium cation.

b. N- α -Metalloce nylalkylation

Many reactions of α -hydroxymetalloce nyl derivatives with different nitrogen-containing nucleophilic agents were performed in the systems *A* and *B*.^{6, 28, 46, 51, 73, 108, 112, 119, 121–124} Both non-ionic (Table 2) and onium (Table 3) organometallic derivatives were synthesised in high yields. In most cases, no special purification techniques were necessary.

Unlike urea (Table 2), thiourea gives only thiouronium salt $\text{FcCH}_2\text{S}^+ = \text{C}(\text{NH}_2)_2\text{BF}_4^-$ in reaction with alcohol **13** in the system *A*.¹⁰⁸

The interaction of aromatic bis-amines (Table 2) with two equivalents of the alcohol **13** and acid HX (system *A*) gave the products of N,N'- α -ferrocenylmethylation, which were isolated in the form of the corresponding salts (Table 2). Under the action of alkali on these salts the elimination of the acid HX and the formation of free bases occurred.¹⁰⁸



Under analogous conditions, the action of two equivalents of the alcohol **13** on urea¹⁰⁸ and the sodium salt of benzotriazole¹¹⁹ the products of N,N'-di- α -ferrocenylmethylation are formed. The same compounds were synthesised in higher yields by the action of the alcohol **13** on the corresponding mono- α -ferrocenylmethylated derivatives under the conditions of system *A* (Tables 2, 3). When the alcohols **26** were used in these reactions, asymmetric products of N,N'-di- α -ferrocenylalkylation of urea, $\text{FcCH}_2\text{NH} \cdot \text{C}(\text{O})\text{NHCH}(\text{R})\text{Fc}$ (R = Me, Ph), were synthesised.⁶ However, the formation of urea derivatives di-substituted at one nitrogen atom, has not been observed, which is presumably due to steric hindrance.

Comparison of the yields (Tables 2, 3) of the structurally similar reaction products reveals that in system *A* they depend only slightly on the nature of the metallocene nucleus, while with increase of the bulk of the substituent at the α -carbon atom (from H to Ph) the yields decrease monotonically.

The correlation between the basicity of the nitrogen-containing derivatives and their capacity to undergo α -metalloce nylalkylation in systems *A* and *B* has been analysed.^{6, 7} In the presence of acid HX or a cation-exchange resin KU-2, the metalloce nylalkylation of the nitrogen-containing nucleophilic compound at the nitrogen atom may also be accompanied by protonation.¹¹⁸ Therefore, the basicity of the nucleophilic substrate is one of the main factors determining the direction and the extent of metalloce nylalkylation.

It is quite clear from the analysis of the results^{6, 7} that nitrogenous bases with $\text{p}K_a > 7$ (ammonia, aliphatic amines) cannot be alkylated in system *A*. Only their protonation at the nitrogen atom

with formation of the corresponding salts occurs with quantitative yields. Compounds with $\text{p}K_a$ between 6 and 4 give the products of N- α -metalloce nylalkylation in poor yields, while the yield of the salts amounts to 80%–85%. The nitrogen-containing substrates with $\text{p}K_a$ value in the range from 4 to –6 react readily with α -hydroxyalkylmetallocenes in system *A* to give high, frequently quantitative, yields (Tables 2, 3) of the corresponding N- α -metalloce nylalkylation products. The formation of salts in this case is not observed. Finally, the extremely weak nitrogen-containing bases with the $\text{p}K_a < -6$ (trinitroaniline, pentachloropyridine) do not enter into the reaction of metalloce nylalkylation in system *A*.⁶

The important role of the solvent is to be emphasised. The use of CH_2Cl_2 and the like allows on the one hand, the synthesis of α -metalloce nylcarbocations in the active form *in situ*, which is due to the low donor activity of CH_2Cl_2 . On the other hand, because of the low solubility of CH_2Cl_2 in water, a two-phase system may be formed, which prevents oxidation of the products of metalloce nylalkylation, which are usually present in the organic phase.

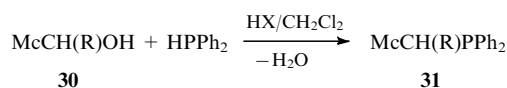
In system *B*, with a 3–5-fold excess of the cation-exchange resin KU-2, compounds with high basicity, such as piperidine and, diethylamine (Table 2), as well as those with low basicity, *e.g.*, 4-bromoaniline or acetamide, readily undergo N- α -ferrocenylalkylation.¹⁰⁴ In this case, the excess of the cation-exchange resin KU-2, ensures the protonation of the highly active nitrogenous compounds and generation of the corresponding electrophilic intermediates from α -hydroxyalkylferrocenes; these intermediates further react with the nitrogen-containing substrates. The shift of the equilibrium of this reaction towards the formation of the alkylation products occurs presumably as a result of efficient desorption of the more hydrophobic N- α -ferrocenylalkylamines from the surface of the cation-exchange resin into the organic phase, dichloromethane.

Thus, the use of the two-phase systems *A* and *B* allows one to perform N- α -ferrocenylalkylation of a variety (Tables 2, 3) of nitrogen-containing nucleophilic compounds with $\text{p}K_a$ spanning a range of more than 15 units.

For the synthesis of biologically active compounds, α -ferrocenylalkylation of nucleotide bases, nucleosides, and DNA has been recently performed under the conditions of system *A*.¹²⁵ α -Hydroxyethylferrocene was used as the alkylating agent; it was possible to introduce α -ferrocenylethyl groups into the molecules of the above-mentioned substrates. According to the analysis of the products, the reaction may follow different routes. The IR and NMR data allow one to suggest that N- α -ferrocenylalkylation occurs at different nitrogen atoms of heterocyclic bases of nucleotide bases, nucleosides and DNA.¹²⁵

c. P- α -Metalloce nylalkylation

Reactions of α -hydroxyalkylmetallocenes with different types of organophosphorus compounds in the two-phase systems *A* and *B* have been studied.^{6, 28, 46, 51, 73, 124, 126} It was found⁶ that in reactions of equimolar amounts of the metallocene alcohols **30** with diphenylphosphine ($\text{p}K_a = -0.20$)¹²⁷ in the system *A*, trisubstituted phosphines **31** were formed as a result of α -metalloce nylalkylation at the phosphorus atom (72%–92%).



Mc = Fc, Rc, Oc; R = H, Me, Ph, CH=CHFc, C $\equiv$ CFc;
X = BF₄, ClO₄.

Unlike diphenylphosphine, diethyl phosphite does not react with the alcohols **30** in system *A*,⁶ however its sodium salt readily reacts with ferrocenemethanol **13** in the two-phase system benzene–aqueous HX⁶ with the formation of the phosphonate **3**, the product of P-ferrocenylmethylation.⁶

Table 2. Reagents, conditions and yields of product (non-ionic compounds) of N- α -metalloenylalkylation in two-phase systems.

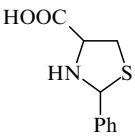
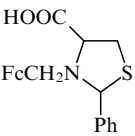
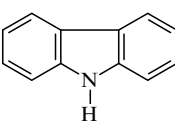
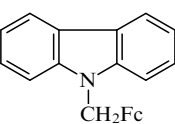
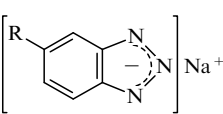
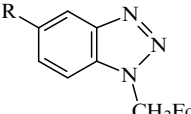
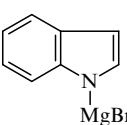
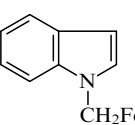
α -Hydroxy-alkylmetal-locene	Nucleophile	Reaction conditions	Reaction time /min	Product	Yield (%)	Ref.
FcCH ₂ OH	NaN ₃	A (CH ₂ Cl ₂ / HX, X = BF ₄ , ClO ₄)	30	FcCH ₂ N ₃	83	108
	H ₂ NC ₆ H ₄ R-4	A (CH ₂ Cl ₂ / HBF ₄)	30 30 30 60	FcCH ₂ NHC ₆ H ₄ R-4	29 (R = H) 18 (R = Me) 87 (R = Br) 96 (R = NO ₂)	108
	H ₂ NC(O)NH ₂	A (CH ₂ Cl ₂ / HBF ₄)	30	FcCH ₂ NHC(O)NH ₂	81	108
	H ₂ NC(O)Me	A (CH ₂ Cl ₂ / HBF ₄)	60	FcCH ₂ NHC(O)Me	37	108
	H ₂ NC(O)Me	B (CH ₂ Cl ₂ / cationite KU-2)	240	FcCH ₂ NHC(O)Me	84	73
	H ₂ NSO ₂ Ph	A (CH ₂ Cl ₂ / HBF ₄)	90	FcCH ₂ NHSO ₂ Ph	70	108
		A (CH ₂ Cl ₂ / HClO ₄)	60		49	108
		A (CH ₂ Cl ₂ / HBF ₄)	15		96	108
		A (CH ₂ Cl ₂ / HX, X = BF ₄ , ClO ₄)	15		96 (R = H) 85 (R = Me) 85 (R = Br) 85 (R = NO ₂)	7, 119
	H ₂ N-Y-NH ₂	A (CH ₂ Cl ₂ / HBF ₄)	75 100 90	[FcCH ₂ NH ₂ ⁺ -Y-NH ₂ ⁺ CH ₂ Fc]2X ⁻	71 (Y = 1,2-Phenylene) 90 (Y = 1,4-Phenylene) 93 (Y = 4,4'-Biphenylene)	108
	FcCH ₂ NHC(O)NH ₂	A (CH ₂ Cl ₂ / HBF ₄)	60	FcCH ₂ NHC(O)NHCH ₂ Fc	78	6
		A (CH ₂ Cl ₂ / HClO ₄)	10		83	112
	4-H ₂ NC ₆ H ₄ N=NPh	B (CH ₂ Cl ₂ / cationite KU-2)	240	4-FcCH ₂ NHC ₆ H ₄ N=NPh	96	73

Table 2 (continued).

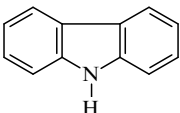
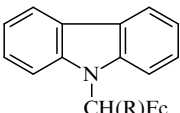
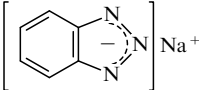
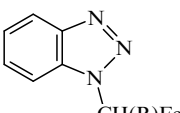
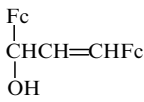
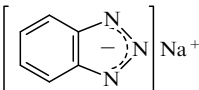
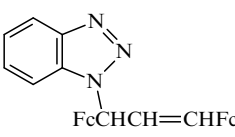
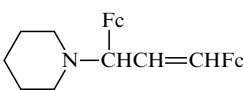
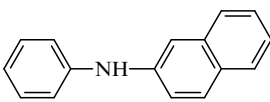
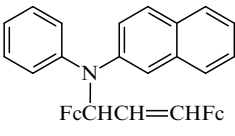
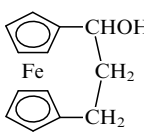
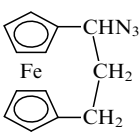
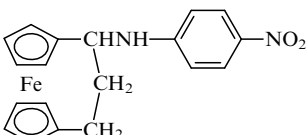
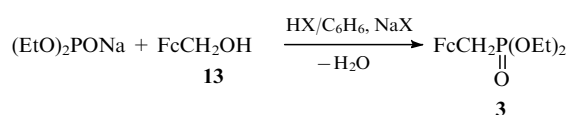
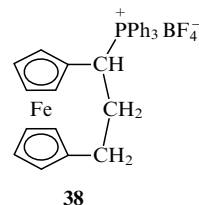
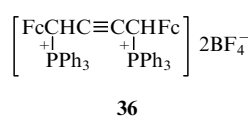
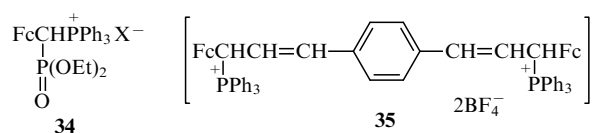
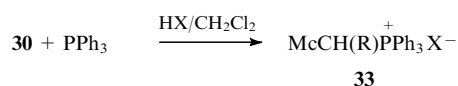
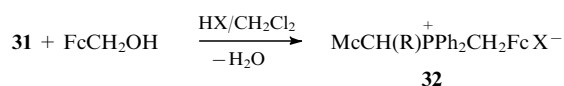
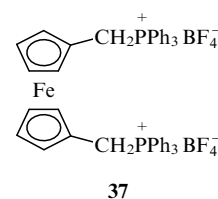
α -Hydroxy-alkylmetal-locene	Nucleophile	Reaction conditions	Reaction time /min	Product	Yield (%)	Ref.
FcCH(R)OH	HNPh_2	<i>A</i> (CH_2Cl_2 / HBF_4)	60	FcCH(R)NPh_2	92 (R = Me) 90 (R = Ph)	108
		<i>A</i> (CH_2Cl_2 / HClO_4)	30		75 (R = Me) 64 (R = Ph)	108
		<i>A</i> (CH_2Cl_2 / HBF_4)	5		96 (R = Me) 80 (R = Ph)	7, 119
	$\text{FcCH}_2\text{NHC(O)NH}_2$	<i>A</i> (CH_2Cl_2 / HBF_4)	60	$\text{FcCH}_2\text{NHC(O)NHCH(R)Fc}$	64 (R = Me) 61 (R = Ph)	6
	KSCN	<i>A</i> (CH_2Cl_2 / HX , X = BF_4 , ClO_4)	60	FcCH(NCS)CH=CHFc	64	46
		<i>A</i> (CH_2Cl_2 / HBF_4)	1200		79	119
	HNEt_2	<i>B</i> (CH_2Cl_2 / cationite KU-2)	120	$\text{FcCH(NEt}_2\text{)CH=CHFc}$	71	73
		<i>A</i> (CH_2Cl_2 / HBF_4)	140		70	73
	$\text{H}_2\text{NC}_6\text{H}_4\text{Br-4}$	<i>A</i> (CH_2Cl_2 / HBF_4)	240	$\text{FcCH(NHC}_6\text{H}_4\text{Br-4)CH=CHFc}$	70	73
	NaN_3	<i>A</i> (CH_2Cl_2 / HBF_4)	150	$\text{FcCH(N}_3\text{)CH=CHFc}$	64	73
		<i>A</i> (CH_2Cl_2 / HBF_4)	180		69	73
	NaN_3	<i>A</i> (CH_2Cl_2 / HClO_4)	30		84	6
	$\text{H}_2\text{NC}_6\text{H}_4\text{NO}_2\text{-4}$	<i>A</i> (CH_2Cl_2 / HBF_4)	60		92	6

Table 2 (continued).

α -Hydroxy-alkylmetal-locene	Nucleophile	Reaction conditions	Reaction time /min	Product	Yield (%)	Ref.
		<i>A</i> (CH ₂ Cl ₂ / HBF ₄)	60		90	6
RcCH(R)OH		<i>A</i> (CH ₂ Cl ₂ / HX, X = BF ₄ , ClO ₄)	15		82 (R = Me) 76 (R = Ph)	112
		<i>A</i> (CH ₂ Cl ₂ / HBF ₄)	150 180		64 (R = Me) 56 (R = Ph)	112
	NaN ₃	<i>A</i> (CH ₂ Cl ₂ / HBF ₄)	30 20	RcCH(R)N ₃	91 (R = Me) 89 (R = Ph)	112
	H ₂ NPh	<i>A</i> (CH ₂ Cl ₂ / HBF ₄)	45 60	RcCH(R)NHPh	54 (R = Me) 55 (R = Ph)	112
	H ₂ NC ₆ H ₄ Br-4	<i>A</i> (CH ₂ Cl ₂ / HBF ₄)	45 60	RcCH(R)NHC ₆ H ₄ Br-4	64 (R = Me) 51 (R = Ph)	112
		<i>A</i> (CH ₂ Cl ₂ / HBF ₄)	60 120		71 (R = Me) 56 (R = Ph)	112

X = BF₄, ClO₄.

The reaction of the tertiary phosphines **31** and triphenylphosphine ($\text{p}K_{\text{a}} = 2.67$)¹²⁷ with different α -hydroxyalkylmetallocenes under the analogous conditions gives the corresponding α -metallocenyl-containing phosphonium salts **32–38** in 60%–100% yields.^{6, 28, 46, 51, 124, 126}

X = BF₄, ClO₄.

The α -metallocenylalkylation of triphenylphosphine with the formation of the corresponding triphenylphosphonium salts **39** readily proceeds also in system *B* in the presence of the salts of alkali metals NaX or KX.⁷³

Table 3. Reagents, conditions and yields of product (onium compounds) of N- α -metallocenylalkylation in two-phase system *A*.

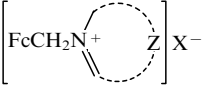
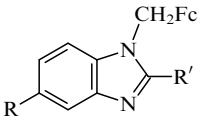
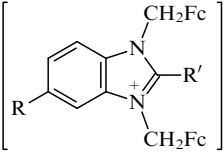
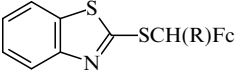
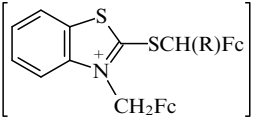
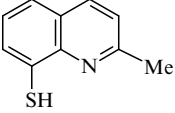
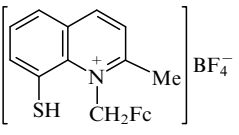
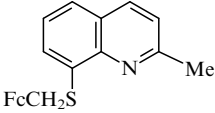
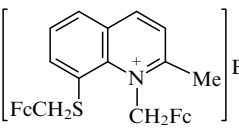
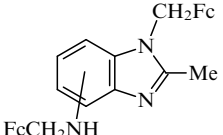
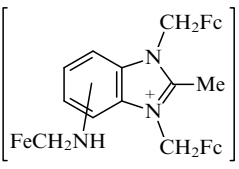
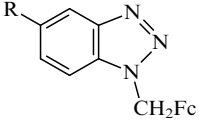
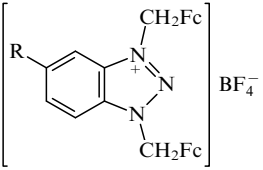
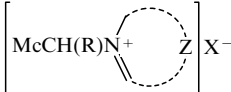
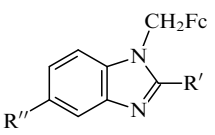
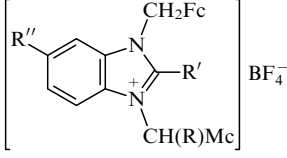
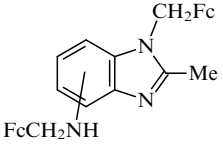
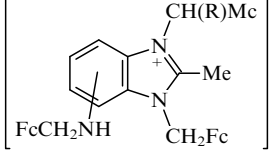
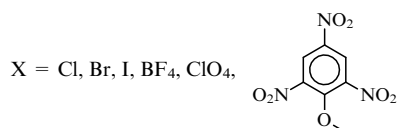
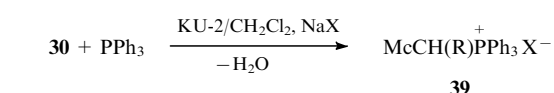
α -Hydroxy-alkylmetal-locene	Nucleophile	Reaction conditions	Reaction time /min	Product	Yield (%)	Ref.
FcCH ₂ OH		CH ₂ Cl ₂ / HX, X = BF ₄ , ClO ₄				
	Pyridine		60	X = BF ₄	100	28
			15	ClO ₄	100	28
	2-Methylpyridine		60	BF ₄	66	121
			30	ClO ₄	77	121
	3-Methylpyridine		60	BF ₄	82	
	4-Methylpyridine		60	BF ₄	37	6
	2-Chloropyridine		60	BF ₄	96	6
	3-Chloropyridine		60	BF ₄	100	6
	4-Chloropyridine		60	BF ₄	100	6
	2,3-Dichloropyridine		60	BF ₄	89	6
	2,5-Dichloropyridine		60	BF ₄	67	6
	Quinoline		30	ClO ₄	100	28
	Isoquinoline		15	BF ₄	72	28
	Lepidine		30	BF ₄	93	121
	2-Methylbenzoxazole		60	BF ₄	100	121
			30	ClO ₄	100	121
	2-Methylbenzothiazole		15	BF ₄	100	121
			15	ClO ₄	100	121
	Hexamethylenetetramine		40	BF ₄	85	28
	Ferrocenyldeneaniline		30	ClO ₄	97	28
		CH ₂ Cl ₂ / HBF ₄	15 40 40		68 (R = R' = H) 65 (R = NO ₂ , R' = H) 62 (R = NO ₂ , R' = Me)	122
		CH ₂ Cl ₂ / HBF ₄	60		82 (R = H) 74 (R = Me) 72 (R = Ph)	122
		CH ₂ Cl ₂ / HBF ₄	20		45	122
		CH ₂ Cl ₂ / HBF ₄	30		63	122
		CH ₂ Cl ₂ / HBF ₄	45		99	122
		CH ₂ Cl ₂ / HBF ₄	5		94 (R = H, Me, Br, NO ₂)	123

Table 3 (continued).

α -Hydroxy-alkylmetal-locene	Nucleophile	Reaction conditions	Reaction time /min	Product	Yield (%)	Ref.
FcCH_2OH		$\text{CH}_2\text{Cl}_2/\text{HBF}_4$	60		99	122
FcCH(Me)OH		$\text{CH}_2\text{Cl}_2/\text{HBF}_4$				6, 28
	Pyridine, 2-Methylbenzothiazole Hexamethylenetetramine		45 35 60		92 71 59	
		$\text{CH}_2\text{Cl}_2/\text{HBF}_4$	5		94	123
		$\text{CH}_2\text{Cl}_2/\text{HBF}_4$	5		93	123
$\text{PhC}\equiv\text{CC}(\text{R})\text{CFc}$ OH		$\text{CH}_2\text{Cl}_2/\text{HBF}_4$				51
	Pyridine Hexamethylenetetramine		60		22 56	
$\text{Fe}(\text{C}_5\text{H}_4\text{CH}_2\text{OH})_2$		$\text{CH}_2\text{Cl}_2/\text{HBF}_4$				73
	Pyridine, 2-Methyl-5-trifluoro- methylsulfonyl-1- -ethylbenzimidazole		90 60		79 56	
$\text{Fe}[\text{C}_5\text{H}_4\text{CH(Me)OH}]_2$		$\text{CH}_2\text{Cl}_2/\text{HBF}_4$				123
	1-Ferrocenylmethyl- benzotriazole Hexamethylenetetramine		5 5		92 94	

Table 3 (continued).

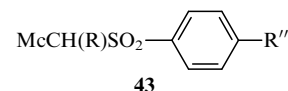
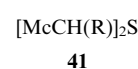
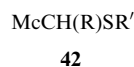
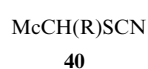
α -Hydroxy-alkylmetal-locene	Nucleophile	Reaction conditions	Reaction time /min	Product	Yield (%)	Ref.
McCH(R)OH		CH ₂ Cl ₂ / HX (X = BF ₄ , ClO ₄)				
	Pyridine		60	X = BF ₄	72 (Mc = Rc, R = Me)	124
	2-Methylpyridine		90	BF ₄	75 (Mc = Rc, R = Me)	
	4-Methylpyridine		90	ClO ₄	52 (Mc = Oc, R = Ph)	
	Lepidine		120	BF ₄	66 (Mc = Oc, R = Me)	
	2-Methylbenzoxazole		45	ClO ₄	75 (Mc = Rc, R = Me)	
	2-Methylbenzothiazole		45	BF ₄	72 (Mc = Oc, R = Me)	
	Benzylideneaniline		180	ClO ₄	48 (Mc = Rc, R = Me)	
	Ferrocenylideneaniline		120	ClO ₄	67 (Mc = Rc, R = Me)	
		CH ₂ Cl ₂ / HBF ₄	30 30 30 60 80 60		100 (Mc = Rc, R = R' = Me, R'' = H) 81 (Mc = Rc, R = Ph, R' = Me, R'' = H) 96 (Mc = Oc, R = R' = Me, R'' = H) 76 (Mc = Rc, R = R' = Me, R'' = NO ₂) 70 (Mc = Rc, R = Ph, R' = H, R'' = NO ₂) 74 (Mc = Oc, R = R' = Me, R'' = NO ₂)	6
		CH ₂ Cl ₂ / HBF ₄	90 120		71 (Mc = Rc, R = Me) 63 (Mc = Os, R = Ph)	6



It should be noted that the triphenylphosphonium salts **33**–**38** and phosphonate **3** may be used as reagents in the Wittig and Horner¹²⁷ reactions for the synthesis of unsaturated compounds of the subgroup VIIIA metallocenes.^{46, 124, 126}

d. S- α -Metallocenylalkylation

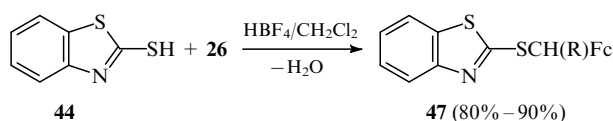
In contrast to CH-acids and nitrogen-containing compounds with an N–H bond, compounds containing SH groups do not react with α -hydroxyalkylmetallocenes in the two-phase systems *A* and *B*.⁶ However the interaction of alcohols **30** with sodium thiocyanate, sulfide, methanethiolate, *N,N*-diethyldithiocarbamate, thiophenoxide, and arenesulfonate in the systems *A* and *B* gives S- α -metallocenyl compounds (**40**–**43**) in 60%–90% yields.^{73, 108, 112}



R = H, Me, Ph, CH=CHFc; R' = Me, Ph, C(S)NEt₂; R'' = H, Me.

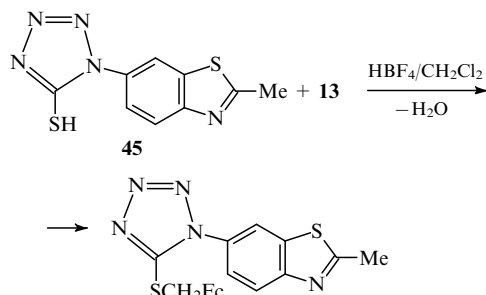
It was estimated by IR-spectroscopy that in the course of reactions with sodium thiocyanate rearrangement products, the corresponding isothiocyanates **40**, are not formed.⁶

The reactions of α -ferrocenylalkylation of the bifunctional nucleophiles **44**–**46** containing both nitrogen and sulfur atoms as two reaction centres with the alcohols **26** in systems *A* and *B* yield the products of both N- and S- alkylation.¹²² Ferrocenylalkylation of 2-mercaptobenzothiazole (**44**) and 2-mercaptobenzimidazole under the action of equimolar amounts of alcohols **26** and HBF₄ occurs at the sulfur atoms in 80%–90% yields.^{7, 122}

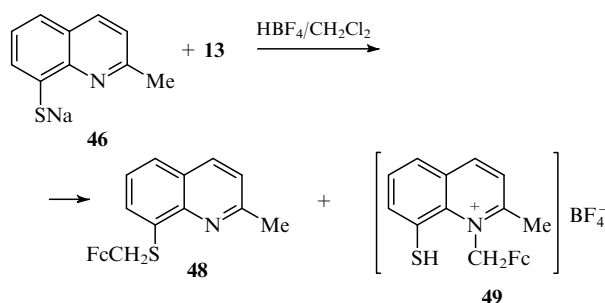


R = H, Me, Ph.

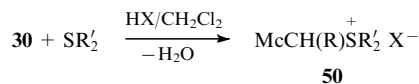
The analogous reaction of *S*- α -ferrocenylalkylation occurs also under the action of ferrocenemethanol **13** on 2-methyl-6-(5-mercapto-1-tetrazolyl)-benzothiazole, **45** but under more rigorous conditions.¹²²



In reactions of equimolar amounts of sodium 2-methylquinoline-8-thiolate **46**, the alcohol **13**, and HBF₄, a mixture of products of ferrocenylmethylation at both sulfur **48** and nitrogen **49** atoms is formed.¹²²



The interaction of sulfides with the alcohols **30** in system *A* leads to *S*- α -metallophenylalkylsulfonium salts **50** in 50%–100% yields.^{28, 51, 124}

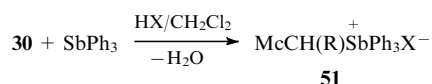


R' = Me, Et, CH₂Ph; X = BF₄, ClO₄.

It has already been mentioned above that, like trialkylferrocenylmethanilium salts, the salts **50** also proved to be efficient α -metallophenylalkylating reagents.^{28, 124}

e. *Sb*- α -metallophenylalkylation

The α -metallophenylalkylation by alcohols **30** of triphenylantimony in the two-phase system *A* has been described.⁶ The triphenylstibonium salts **51** are formed in this reaction.



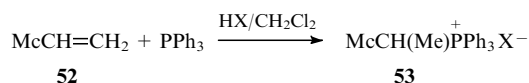
Mc = Fc, Rc, Oc; R = H, Me.

It turned out that the yields of the salts **51**, in contrast to the triphenylphosphonium salts, depend to a considerable extent on both the size of the substituents R at the α -carbon atom and on the size of the metal atom in the metallocene core. Increase in the steric hindrance lowers the yields from 74% to 17%;⁶ in the case of hydroxy derivatives of ruthenocene and osmocene and R = Ph the triphenylstibonium salts are not formed at all.⁶

f. α -Metallophenylalkylation by vinylmetallocenes

Similarly to the α -hydroxyalkylmetallocenes, vinyl derivatives of ferrocene, ruthenocene, and osmocene **52** may be also successfully used in α -metallophenylalkylation reactions^{6, 115, 124} for the synthesis of the same products. For instance, in systems *A* and *B*^{6, 115} 2,3-diferrocenylbutane was obtained in the presence of powdered copper in 70%–72% yields (see Table 1), while the interaction of alkenes **52** with triphenylphosphine in the system *A* leads to the

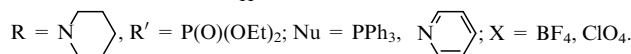
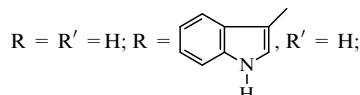
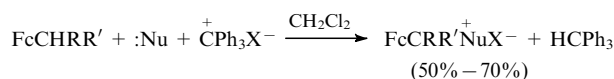
corresponding triphenylphosphonium salts **53** with 80%–95% yields.^{6, 124}



X = BF₄, ClO₄.

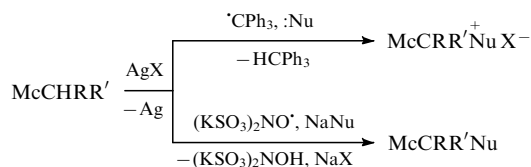
V. α -Hydrogen-containing metallocenes in α -metallophenylalkylation reactions

New methods of α -metallophenylalkylation of nucleophilic substrates with the use of α -hydrogen-containing metallocene derivatives as alkylation agents have been proposed.^{6, 74, 128} For instance, the action of triphenylcarbenium salts on an equimolar mixture of α -hydrogen-containing derivatives of ferrocene and nucleophile in anhydrous dichloromethane gives the corresponding products of α -ferrocenylalkylation and triphenylmethane in high yields.^{6, 128}

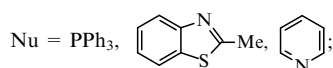


However, the α -hydrogen-containing ruthenocene and osmocene derivatives turned out to be unreactive.⁶

A more general method of α -metallophenylalkylation of nucleophilic compounds by α -hydrogen-containing metallocene derivatives of subgroup VIIIA was proposed by Boev.⁷⁴ The essence of this method is as follows: at first, α -hydrogen-containing derivatives of metallocenes are treated with oxidizing agents (AgClO₄, AgBF₄, FeCl₃) in dichloromethane, then an equimolar mixture of a free radical (triphenylmethyl or Fremy's salt¹²⁹) and a nucleophilic substrate is added to the oxidation products. As a result, the products of substitution of the α -hydrogen atom by a nucleophile are formed with high yields. In the case of the use of Fremy's salt (KSO₃)₂N–O• and anionic nucleophiles (NaNu), the second step of the process is performed in a two-phase system CH₂Cl₂–H₂O with intense stirring at room temperature.^{6, 74}



Mc = Fc, Rc, Oc; R = R' = H; R = H, R' = Me; R = H, R' = Ph;



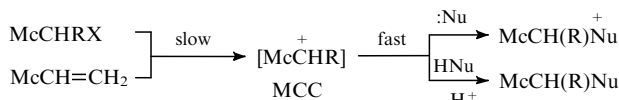
Nu[−] = CN[−], N₃[−], PhS[−], PhO₂S[−]; X = BF₄, ClO₄.

Along with the target products, triphenylmethane (in 86% to 94% yield) or potassium hydroxylamine disulphonate (in 80% to 90% yield) were isolated.

VI. On the mechanism of α -metallophenylalkylation reactions

The analysis of literature data^{3–11} reveals that all reactions of α -metallophenylalkylation proceed *via* the formation of thermally stable ^{3,5} α -metallophenylcarbocations (MCC), the mechanism of their formation depending on both the nature of the initial

substrates and on the reaction conditions. The MCC then react quite rapidly with the nucleophilic reagents to yield the products of α -metallocenylalkylation. Some researchers^{3,8,10,17} believe that the mechanism of these reactions may be classified as S_N1 .



$X = \text{NMe}_3^+, \text{SMe}_2^+, \text{Hal}, \text{OH}; \text{Mc} = \text{Fc}, \text{Rc}, \text{Os}.$

Unfortunately, no special kinetic studies that would confirm the formation of MCC as a kinetically independent species corresponding to a definite point on the reaction coordinate have been performed so far, but a series of indirect experimental data support an S_N1 mechanism.

In particular, it has been shown by numerous experiments,^{6,7} that α -metallocenylalkylation in the two-phase systems *A* and *B* may proceed only at the interface of phases with high acidity ($H_0 \approx -7$ to -9).¹⁰⁹ It is under these conditions that the generation^{3,5} of metallocenylcarbocations from α -hydroxyalkyl- and α -alkenylmetallocenes readily occurs. In this case, the proton is thought to attack the oxygen atom of the hydroxyl group or the double bond as centres with the highest nucleophilicity in the substrates.

Attack of the proton at the metallocene fragment is also possible, as it is known¹⁻³ that ferrocene, ruthenocene, and osmocene, under certain conditions, can be protonated. It has however been established by Boev,⁶ that these metallocenes practically do not undergo any changes under the action of aqueous acids HX ($X = \text{BF}_4, \text{ClO}_4$) or a cation-exchange resin KU-2 in systems *A* and *B* (according to UV and NMR data), while in the presence of nucleophilic reagents only the salts of the latter are formed. Besides, as has been mentioned above, the metallocene nucleus in the two-phase systems is in the organic phase and therefore it is inaccessible to protons. Therefore, initial attack of the proton at the metal atom, as the potential basic centre in organometallic substrates in the two-phase systems *A* and *B*, may be excluded.

On the other hand, the action of aqueous acids HX on α -hydroxyalkylmetallocene derivatives^{6,108} and vinylferrocene⁶ in dichloromethane in the absence of the nucleophilic substrates results in the quantitative formation of MCC (according to UV-spectral data), identified by comparison with the authentic^{95,124} species. Therefore, high acidity of the medium, that arises at the interface in the system *A* guarantees the efficient formation of the corresponding MCC from vinylferrocene and ferrocenyl-alkanols. The study of the reactions of the authentic MCC with different nucleophiles has shown that they lead to formation of the corresponding derivatives of FcCHRNu type with quantitative yields.⁶

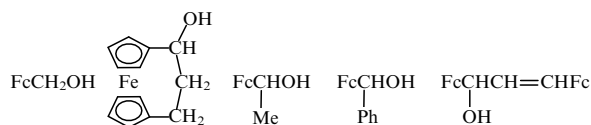
All these data indicate that MCC correspond to a definite point on the reaction coordinate of metallocenylalkylation.

In the two-phase system *B* (liquid–solid phase), the formation of MCC may occur only at the surface of KU-2 in the H-form. This is indirectly confirmed by the fact that the rate and the yield of the reaction of α -metallocenylalkylation in the system *B* are directly affected by the intensity of mixing of the reaction system, that is by the efficiency of the contact of the reacting substrates with the surface of the cation-exchange resin KU-2, where the MCC is generated.^{6,73}

The observation⁷³ (both visual and microscopic) of the resin surface during the reaction leads also to the conclusion of possible generation of MCC at its surface. At first, the resin grains change their colour from light-brown to dark-red or dark-blue, which is characteristic of MCC,³ and then as the MCC formed react with nucleophiles, the initial light-brown colour is restored.

The comparison of the rate of reactions of the ferrocene-containing alcohols of different structural types with aqueous solutions of HX and triphenylphosphine (system *A*) by the

method of competing reactions¹²⁴ demonstrates that the activity of alcohols in alkylation reactions decreases with the increase in the steric hindrance at the α -carbon atom independently of the thermodynamic stability (pK_{R^+}) values of the corresponding carbocations.³

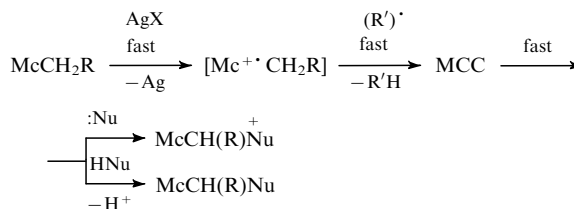


$pK_{R^+} \quad -1.75 \quad -3.20 \quad -0.92 \quad -0.15 \quad +4.18$

The activity of the structurally similar alcohols of ferrocene, ruthenocene, and osmocene decreases with decrease in the pK_{R^+} of the corresponding carboxylic acids in the following series:¹²⁴ $\text{OcCH(Me)OH} (+1.75) > \text{RcCH(Me)OH} (+1.20) > \text{FcCH(Me)OH} (-0.92).$

The generation of MCC from α -hydrogen-containing metallocene derivatives in reactions of α -metallocenylalkylation of nucleophiles presumably proceeds in a different way. In this case, MCC are formed as a result of the oxidative dehydration of α -hydrogen-containing metallocene derivatives subjected to the action of the triphenylcarbocation salts.¹³⁰

An analogous mechanism is presumably realised in the reaction of the α -hydrogen-containing metallocene derivatives first with an oxidant and then with a mixture of the stable radical with a nucleophile.⁷⁴



$(\text{R}')^\cdot = \text{Ph}_3\text{C}^\cdot, (\text{KSO}_3)_2\text{NO}^\cdot.$

Thus, the reactions of α -metallocenylalkylation of nucleophilic reagents may proceed according to two alternative mechanisms depending on the nature of the initial reagents and the reaction conditions.

One of them, the S_N1 mechanism, is realised in reactions of ammonium,³ and sulfonium¹²⁴ salts, or of α -halogen derivatives³ of metallocenes with the nucleophilic reagents, or in reactions of α -hydroxy or α -alkenyl derivatives of metallocenes with acids HX or a cation-exchange resin in the two-phase systems *A* and *B*.^{6,7}

Another mechanism, $S_{RN}2$,^{4,6} is involved in the consecutive interaction of α -hydrogen-containing metallocene derivatives with one-⁷⁴ or two-electron¹²⁸ oxidizing agents, and then with nucleophiles as the reducing agents.

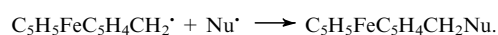
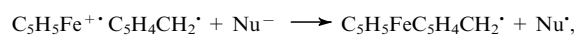
While discussing the mechanism of reactions of α -ferrocenylalkylation, one should not neglect the possible contribution of free-radical and redox processes, if only because of easy oxidizability of the ferrocene nucleus in acidic media in the presence of oxygen. These processes can in general be initiated in at least two ways, either through protonation and further oxidation of the central atom or by migration of an electron from the central metal atom to the carbenium centre.

As has been mentioned earlier in connection with the reactions proceeding in system *A*, the first way seems improbable, because the reaction centre (in this case the iron atom), located in the organic phase, is shielded from proton attack by the interface. Such shielding occurs in systems of *B* type, the difference, however, is that the carbenium centre is located in the adsorption layer of the cation-exchange resin. However, in those cases the reaction proceeds in a single-phase system, especially in the presence of strong acids, the contribution of protonation at the main metal centre may become significant.

As to the second reaction pathway, the general possibility of the migration of an electron from iron to the carbenium α -carbon with the formation of a paramagnetic compound has been unambiguously demonstrated in the example of the diamagnetic nonamethylferrocenylcarbenium salt.¹³¹ It has also been demonstrated that the biradicals thus formed may recombine, to give the corresponding binuclear dications.¹³¹ It has also been found that phenylferrocenylcarbenium tetrafluoroborate undergoes the analogous transformations. In this case as well, the dication is formed, which may be reduced to 1,2-diphenyl-1,2-diferrocenylthene.[‡] The doublet states E_{2g} and A_{1g} are close in energy, thus ensuring the possibility of the thermal occupation of the d_{z^2} iron orbital and facilitating electron transfer from iron to the carbon atom without disturbance of the orbital symmetry.¹³² Taking these facts into account, formation of ferrocenium salts and diferrocenylalkanes in reactions of α -ferrocenylalkylation may be regarded as indirect evidence for realisation of the pathway initiated by electron transfer from iron to carbon atoms.

In the two-phase systems, where reactions usually proceed with quantitative yields, the contribution of the reaction following this pathway is rather small. Nevertheless, it becomes noticeable when reactions are performed under more drastic conditions, which is in agreement with the increase of the yield of the side products of dimerisation and polymerisation.

Some ferrocenium salts may oxidise some nucleophiles, especially anions (*e.g.*, azole anions).¹³³ It cannot be excluded that the final products of ferrocenylalkylation in certain situations may be formed according to the free-radical scheme with initiation by single-electron transfer:



In this case, realisation of the redox mechanism results not only in dimerisation and polymerisation products, but also leads to the target products.

On the other hand, in Ru and Os compounds, the formation of direct metal- α -carbon contact and the corresponding onium derivatives, which has been demonstrated recently,¹³⁴ should most likely result in blocking of the reaction centre and decrease

in the reactivity in α -metallophenylalkylation. In these systems the contribution of redox processes seems highly improbable.

VII. Conclusion

The data of the present review demonstrate, that during recent years many studies aimed at both the extension of known and the search for the new methods of α -metallophenylalkylation of different nucleophilic reagents have been carried out. At present a vast variety of different ferrocenylalkylating reagents is used, *viz.*, ferrocenylalkylammonium salts and the like (especially, the corresponding pyridinium salts), ferrocenylsulfonium salts, α -haloalkyl ferrocene derivatives, α -hydroxyalkyl-, as well as α -alkenyl derivatives of metallocenes. It allows one to perform reaction at quite different reactivity centres (N-, C-, O-, S-, P-). The use of various additives (oxidative, acid-base, radical) offers further possibilities.

The synthetic potential is considerably extended by metallophenylalkylation in liquid-liquid or liquid-solid two-phase systems. In these systems most reactions proceed under mild conditions with high yields of the final products, which often do not require special purification. This allows one to overcome the limitations associated with the acid-base characteristic of the nucleophilic reagents. Besides, the use in these systems of the ferrocene-containing alcohols allows one not only to work with stable initial reagents, but also to vary considerably the substituents at the α -carbenium centre. The advantages of the two-phase systems are illustrated in Table 4, in which the possibilities and conditions of α -ferrocenylalkylation reactions are compared.

The variety of methods of ferrocenylalkylation allows one to perform the synthesis of different functionally substituted derivatives of ferrocene and other α -metallophenyl compounds of subgroup VIIIA metals.

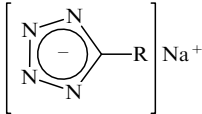
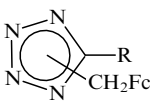
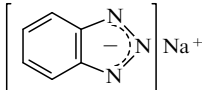
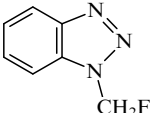
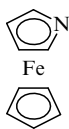
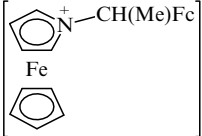
The practical use of these compounds is rather extensive.³ Many of the newly synthesised α -ferrocenylalkyl compounds may be of interest as medicinals with antimicrobial,^{136–142} antiinflammatory,^{143, 144} antitumor,^{6, 7, 145–149} activity as well as chemical means of plant protection.¹⁵⁰ Photosensitive materials with α -ferrocenylalkyl compounds as electron-donating components^{151–155} or organic photoconductors¹⁵⁶ have been developed. A series of ferrocene derivatives of this class found application as stabilisers of rubbers,¹⁵⁷ latent image centres in high-resolution photographic materials,¹⁵⁸ regulators of burning

‡ L. V. Snegur, unpublished data.

Table 4. α -Ferrocenylalkylation of nucleophile compounds.

Ferrocenyl-alkylating reagent	Nucleophile	$T/^{\circ}C$	Time /h	Solvent	Additional conditions	Type of product	Yield (%)	Ref.
[FcCH ₂ NMe ₃] ⁺ I [−]	NH ₂ NHPh	100	1	H ₂ O	NaOH	FcCH ₂ NHNHPh	80	18
	Na ₂ S	100	1	H ₂ O		FcCH ₂ SCH ₂ Fc	54	135
	(EtO) ₂ PONa	138	17	<i>p</i> -Xylene		FcCH ₂ P(O)(OEt) ₂	45	18
	C ₆ H ₅ NH ₂	100	1.5	H ₂ O		FcCH ₂ NHC ₆ H ₅	75	135
FcCH ₂ NMe ₂	(CH ₃ CO) ₂ O	100	20	–	Sealed tube	FcCH ₂ OCOCH ₃	89	135
[FcCH ₂ NMe(CH ₂) ₃] ⁺ SO ₃ [−]	NaN ₃	100	0.03	H ₂ O		FcCH ₂ N ₃	98	27
	NH ₄ OH	20	15	C ₆ H ₆		FcCH ₂ NH ₂	30	27
	NH ₄ OH	60	2	C ₆ H ₆		FcCH ₂ NH ₂	30	27
[FcCH ₂ SMe ₂] ⁺ BF ₄ [−]	NaN ₃	100	1	H ₂ O		FcCH ₂ N ₃	90	28

Table 4 (continued).

Ferrocenyl-alkylating reagent	Nucleophile	$T/^{\circ}\text{C}$	Time /h	Solvent	Additional conditions	Type of product	Yield (%)	Ref.
FcCH_2Cl (without isolation)		56	4–6	Acetone	N_2		Not indicated	37, 38
	$\text{H}_2\text{NC(O)NH}_2$	70	7	Acetone	N_2	$\text{FcCH}_2\text{NHC(O)NH}_2$	29	39
$[\text{FcCHPh}]^+ \text{BF}_4^-$ (freshly prepared)	NaCN	20	0.08	CH_2Cl_2		FcCH(Ph)CN	90	95
FcCH_2OH	PPh_3	20	1	CH_2Cl_2	$[\text{Ph}_3\text{C}]^+ \text{BF}_4^-$	$[\text{FcCH}_2\text{PPh}_3]^+ \text{BF}_4^-$	95	73
		20	1	CH_2Cl_2	$\text{HBF}_4/\text{H}_2\text{O}$	$[\text{FcCH}_2\text{PPh}_3]^+ \text{BF}_4^-$	100	28
	$\text{C}_5\text{H}_5\text{N}$	20	1	CH_2Cl_2	$\text{HBF}_4/\text{H}_2\text{O}$	$[\text{FcCH}_2\text{NC}_5\text{H}_5]^+ \text{BF}_4^-$	100	28
		20	0.08	CH_2Cl_2	$\text{HBF}_4/\text{H}_2\text{O}$		95	7, 119
	Na_2S	20	0.5	CH_2Cl_2	$\text{HBF}_4/\text{H}_2\text{O}$	$\text{FcCH}_2\text{SCH}_2\text{Fc}$	93	108
FcCH(Me)OH	FcH	20	0.05	CH_2Cl_2	$\text{HBF}_4/\text{H}_2\text{O}$	FcCH(Me)Fc	60	114
		20	0.08	CH_2Cl_2	$\text{HBF}_4/\text{H}_2\text{O}$		93	123

processes,¹⁵⁹ macroenergetic compounds,¹⁶⁰ and indicators of radioactivity.⁶

Taking into account the dynamics of the development of the synthetic and applied studies in this field of organometallic chemistry, one may anticipate the elaboration of technological aspects of ferrocenylalkylation reactions, new investigations leading to α -metallocenylalkyl compounds of various structures that may find extensive applications in different fields of science, technology, medicine, and agriculture.

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Immobilisation of analytical reagents on support surfaces

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Abstract. The use of analytical reagents immobilised on the surface of sorbents in sorption-spectroscopic methods of analysis is surveyed. The bibliography includes 131 references.

I. Introduction

At present, analytical methods which can be used not only under stationary laboratory conditions, but also at the site of sampling are attracting more and more attention of researchers.^{1,2} These methods should be highly sensitive and selective and also permit quick, easy and cheap analysis. Determination of traces of substances is preceded, as a rule, by their extractive concentration, ion-exchange separation,^{3,4} etc. It is known³ that efficient extraction of traces of elements by a small volume of an organic solvent from a large volume of the aqueous phase is hampered by the mutual solubility of these phases and by the difficulty of their separation. Ion-exchange materials are used most frequently for separation rather than for concentration of substances,⁵ because, prior to the analysis, the absorbed ions must be eluted, and this implies dilution and, hence, decreases the sensitivity of the analysis. Better results can be achieved by measuring an analytical signal of the analyte directly on the surface of an ion-exchanger or another sorbent.⁶

There is a linear correlation between the absorption of light by a solid sorbent and the concentration of a substance adsorbed on its surface.⁷ The method based on this correlation, which is referred to as solid-phase spectrophotometry, permits the sensitivity of analysis to be increased substantially compared to that achieved when the light absorption of the analyte is measured after its elution to a solution. Currently, sorption-photometric, sorption-luminescence and sorption-X-ray fluorescence techniques are being successfully developed; the procedures include concentration of the component to be determined from the liquid or gaseous phase onto a solid matrix, which is accomplished by its reaction with a reagent fixed on the surface, and subsequent measurement of spectral characteristics of the solid phase, in particular, of its reflection coefficient. Equations relating the

diffuse reflection coefficient of a matrix to the concentration of a substance adsorbed on its surface for thick layers of finely dispersed weakly absorbing samples (Kubelka–Munk function) and for a thin adsorbent layer (for example, for paper chromatography) have been proposed.^{8–10} The measurements can be carried out directly on the surface of the sorbent.

Sorption concentration in combination with measurement of an analytical signal on the surface makes it possible to decrease the limits of detection of elements by several orders of magnitude,^{5,8–11} while the use of sorbents modified by specific analytical reagents increases the selectivity of analysis.

Sorbents modified with chromophoric reagents are used in visual test methods which are indispensable for quick analysis of environmental objects, especially, for tentative (rough) analysis.^{1,2}

To transfer an analyte to the sorbent phase, various procedures are used: (a) the ion to be determined is first absorbed by an ion-exchange resin and then ‘visualised’ by a reagent that forms a coloured compound with the sorbate; (b) the analyte is converted initially into a complex by interaction with an organic or inorganic reagent or into an ion associate in solution, and then it is sorbed by an ion exchanger or by a non-modified sorbent; (c) the analyte is extracted from solution by a sorbent modified with an appropriate organic or inorganic analytical reagent. The latter method is the most promising, especially for the environmental control, for two main reasons. Firstly, the formation of a coloured compound in the sorbent phase is less dependent on the ionic strength of the solution than that in the solution bulk. Secondly, the reagent, which has an influence on the chemical equilibrium in the system under analysis, virtually does not pass from the sorbent surface to the aqueous phase.

In recent years,¹² it has been shown that chemical and analytical properties of immobilised reagents, especially the complex-forming ability, often differ markedly from those in solution. The chemical interactions in a two-phase system ‘an analyte in solution—an analytical reagent fixed on the surface of a solid support’ have not been adequately investigated.

Thus, the use of organic reagents fixed on a solid matrix is a new line in modern analytical chemistry that develops at the boundary between the analytical chemistry and surface chemistry.

II. Classification of modified sorbents

Sorbents modified with various reagents and meant for analytical purposes can be classified according to the type of either the support or the modifying agent used. Various sorbents are used as supports: ion-exchange resins, cellulose, poly(vinyl chloride)

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membranes, fibres and, most frequently, highly dispersed silicas.^{3, 13} Chelate-forming organic reagents,^{15–41} metal salts,^{42–46} natural compounds^{47–50} and some micro-organisms^{51, 52} have found the widest application as modifiers.

The possibilities of the target-directed variation of the chemical and analytical properties of sorbents by modifying them with various reagents are almost limitless. A number of techniques can be used to fix an analytical reagent on a matrix. One of them is a synthetic method involving the so-called covalent grafting of a modifying reagent.⁵³ Another method is impregnation of a matrix with a solution of a modifier.⁵⁴ The most convenient way consists in immobilisation (or fixing) of a modifying reagent on the surface of a support using adsorption, electrostatic interaction, hydrogen bond formation or other types of interaction.^{12, 55}

The main advantage of modified sorbents prepared *via* covalent grafting is their chemical and mechanical stability. Difficulty and complexity of modification and regeneration of systems of this type should be regarded as their drawbacks.

Impregnation of sorbents with analytical reagents is much less labour-consuming. However, the resulting sorbents are not very suitable for operation under dynamic conditions and are relatively unstable; therefore, they do not ensure sufficient reproducibility of analytical results.

At present, there exists a broad range of sorbents with analytical reagents immobilised on their surface. They are chemically and mechanically stable and are easily modified and regenerated. Sorbents of this type are best suited to the requirements for visual test systems.

III. Methods for the immobilisation of analytical reagents

1. Sorption of organic reagents from polar aprotic and protic solvents

This method is used most frequently for immobilisation of reagents under both static and dynamic conditions. Water, acetone, dimethylformamide, alcohols and their mixtures with water are used as solvents. Some examples of modification of sorbents by this method are presented below.

Silica gel has been modified with 8-hydroxyquinoline (HQ) by stirring the sorbent, first, with formaldehyde and acetic acid for 1 h and then with a solution of HQ in anhydrous ethanol for 2 h at 60 °C.^{24, 56}

Immobilisation of 1-(2-pyridylazo)-2-naphthol (PAN) on silica gel has been carried out under static conditions by stirring an ethanolic solution of the reagent with a weighed portion of the sorbent for 4 h.⁴⁰ The modified sorbent was washed with water and dried for 12 h at 80–100 °C and then for several hours at 80 °C under reduced pressure. The content of PAN in silica gel obtained in this way was $4 \mu\text{mol g}^{-1}$. When silica gel was modified under dynamic conditions,⁵⁷ a solution of PAN in a 2 : 8 ethanol–water mixture was passed through a column with the sorbent using a peristaltic pump or a syringe.⁵⁷ The excess of the reagent was removed by elution with a solution of HNO_3 .

Immobilisation of PAN on the surface of a styrene-divinylbenzene copolymer has been carried out in static and dynamic regimes from a methanolic solution.⁵⁸

To modify silica gel with Eriochrome Black T, an ethanolic solution of a modifier was poured over a weighed portion of the sorbent, and the mixture was stirred with a magnetic stirrer for 30 min, and then filtered, washed with water and dried.⁵⁹ Modification of silica gel with polyhydroxyflavones has been carried out in a similar way.⁶⁰

4-(2-Thiazolylazo)resorcinol (TAR) has been applied on the surface of Silochrome C-120 from acetone solutions.⁶¹ The Silochrome was treated with 1 M solution of sulfuric acid and washed with water to create a weakly acidic medium. After that, a solution of TAR was introduced, and the system was allowed to stand for 1 day with occasional stirring. The sorbent was washed with water and dried in air.

Organic reagents have also been applied from aqueous solutions. For example, to modify the AB-17 $\times 8$ anion exchanger with 1-(2-thiazolylazo)-2-naphthol-3,6-disulfonic acid (TAN-3,6-S), a weighed portion of the sorbent was shaken for 30 min in an aqueous solution of the reagent at pH 5.7. The modified ion exchanger was washed with water and dried in air.^{62, 63}

Membrane ultrafilters have been modified by immersing them in a mixture of water with a solution of the corresponding organic reagent in dimethylformamide (DMF).⁶⁴ The optimum time needed for the modification of the poly(vinyl chloride) film 'Vladipor' with 4,4'-bis(dimethylamino)thiobenzophenone from a 50% DMF solution was only 10–15 min.⁶⁵ The modified films were thoroughly washed and stored in the dark in twice distilled water.

Sorption of a chemiluminescent reagent lucigenin on the surface of various silicas has been carried out from aqueous solutions.^{55, 66} The maximum uptake was achieved on non-functionalised silicas, silica gel ($1.6 \times 10^{-5} \text{ mol g}^{-1}$) and Silpearl ($3.4 \times 10^{-5} \text{ mol g}^{-1}$), over a period of 5 min.

2. Sorption of organic reagents from non-polar aprotic solvents and their mixtures

Modification of silica gel with quaternary ammonium salts has been carried out as follows. Silica gel was stirred with a solution of a reagent in hexane for 1 h and then dried for 2 h at 60 °C.^{67, 68}

Static modification of silica gel with di(2-ethylhexyl) phosphate (DEHPA) has been carried out by stirring the sorbent, dried preliminarily for 2 h at 160 °C, with a solution of DEHPA in a chloroform–heptane mixture (70 : 30).³⁷ Then the sorbent was dried in air until the solvent was completely removed.

A similar procedure was used to modify silica gel with the azanalogue of dibenzo-18-crown-6; for this purpose, a solution of the crown compound in a heptane–chloroform mixture (1 : 1) was employed.⁶⁹

3. Immobilisation of organic reagents from the gas phase

A method for the modification of sorbents by treating them in a high-frequency low-temperature plasma in the presence of vapours of organic reagents has also been proposed.⁷⁰ Polysorb-1 was used as the sorbent and propargyl alcohol, allylamine and acrylic acid were used as modifiers. The sorbents were treated for 30 min, and after that, they were washed twice with methanol by decantation and dried in air.

4. Immobilisation of inorganic reagents

Modification of sorbents with inorganic reagents is mostly carried out by sorption or precipitation of metal hydroxides, oxides or salts on their surface.

Immobilisation of calcium phosphate on silica gel has been performed by treatment of the sorbent with a solution of calcium hydroxide and, after drying, with a solution of sodium dihydrogen phosphate.⁷¹ Then the material was dried once again.

Aluminium and iron hydroxides have been applied to the surface of activated carbon by precipitating them from a solution of the corresponding sulfate in the presence of coagulating agents based on polyacrylamide.⁷²

To apply titanium and zirconium hydroxides on carbon, it has been preliminarily impregnated with solutions of salts of these metals; then the hydroxides have been precipitated with ammonia, and the sorbent dried in air at 105–115 °C.^{73, 74}

The modification of acetylcellulose by manganese oxide has been accomplished by treating the sorbent with a solution of potassium permanganate at 60 °C and pH 2.⁷⁵

5. Composite materials based on modified sorbents

Modified sorbents serve as the basis for a number of composite materials.⁷⁶ For example, a composite material based on polyacrylonitrile fibre has been filled during moulding with a selective chelate-forming sorbent containing grafted heterocyclic amines⁷⁷ or with a strongly basic anion-exchange resin.⁷⁸ Discs of a

polyacrylonitrile fibre filled with finely dispersed ion exchanger have been additionally modified by immersing them into a solution of PAN in aqueous acetone⁷⁹ or into aqueous solutions of Xylylene Orange (XO),⁸⁰ arsenazo I⁸¹ or *p*-nitrosodiethylaniline.⁸² The resulting materials were stored wet.

Immobilisation of 4-phenylazo-3-aminorhodanine (PAAR) to a disc-shaped polyacrylic fibre filled with a finely dispersed KU-2 ion-exchange resin has been carried out in the following way.⁸³ Wet discs weighing 40–50 mg were washed with 50 ml of 0.1 M HNO₃ and with 10 ml of acetone, immersed into 10 ml of a 5×10^{-5} M solution of PAAR for 15 min and washed with 50 ml of 0.1 M H₂SO₄. The material was stored wet. The capacity of the sorbent with respect to PAAR was 5×10^{-6} mol g⁻¹.

IV. Analytical applications of modified sorbents

1. Organic reagents

a. Nitrogen-containing reagents

Sorption of gaseous compounds — hydrogen sulfide, carbon disulfide, methanethiol and sulfur dioxide — on silica gel impregnated with diethanol- and monoethanolamine has been studied.⁸⁴ The capacity of the sorbent with respect to diethanolamine amounted to 1.51–2.06 mmol g⁻¹. The sorption of gases is due to their chemical interaction with amines. Unlike acidic gases, CH₃SH is inert towards monoethanolamine and diethanolamine; therefore, it is adsorbed on modified silica gel much less efficiently than on the pure support.

A procedure for the determination of traces of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) in river water and in industrial sewage has been developed.²³ The method involves preliminary sorption of the metal cations on silica gel impregnated with *N,N,N',N'*-tetrakis(2-aminophenyl)ethylenediamine and their subsequent desorption with a 0.13 M solution of tartaric acid at pH 3. The contents of metals are determined by spectrophotometry. The calibration plots are straight lines for concentrations of the metal ions ranging from 1×10^{-8} to 3×10^{-6} mol litre⁻¹.

It has been proposed to use *p*-nitrosodiethylaniline immobilised on discs of a polyacrylonitrile fibre filled with the strongly acidic KU-2 cation-exchange resin as a unit sensitive to the presence of Pd(II) ions.⁸² Palladium ions are sorbed from solutions in a dynamic regime, and diffuse reflection spectroscopy is used for their determination. The response of the sensing element is formed over a period of 2–10 min at a palladium(II) concentration of 1×10^{-6} mol litre⁻¹, and the detection limit is 5×10^{-9} mol litre⁻¹. The use of immobilised *p*-nitrosodiethylaniline makes it possible to improve the selectivity and enhance the sensitivity of the determination of palladium and to extend the range of concentrations suitable for determination compared to that in the case of conventional photometric analysis.

The possibility of concentrating and determining Zn(II) and Cd(II) ions with the aid of an ion exchanger modified with phenylsulfonfylaminoquinoline, which is fairly sensitive and relatively selective with respect to these metals, has been studied.⁸⁵ The contents of metal ions were determined by fluorometry.

A new solid-phase chemiluminescence reagent for the determination of V(IV) and Fe(II) ions has been obtained based on lucigenin (*N,N*-dimethyldiacridylum nitrate) immobilised on a silica gel or Silpearl surface.^{55, 66} The limit of detection of V(IV) is 0.7 and that for Fe(II) is 0.8 mg litre⁻¹. One portion of the reagent makes it possible to carry out more than 200 analyses in a flow regime without additional regeneration.

An extraction and chromatographic procedure involving the use of silica gel modified with Aliquat 336S has been proposed for the determination of bismuth at pH 3 in a 0.01 M solution of citric acid.⁸⁶ At the final stage, bismuth is determined by spectrophotometry as an iodide complex. The procedure is suitable for the determination of bismuth in low-melting alloys containing also lead, zinc, antimony and tin.

A simple and rapid method for concentrating zinc ions as a complex with 4-(2-pyridylazo)resorcinol (PAR) using methyl-

triocetylammmonium chloride and bromide immobilised on the surface of biphenyl with PAR has been proposed.⁸⁷ The content of zinc was determined by the atomic absorption method.

Sorption of high-molecular-weight quaternary ammonium bases on highly dispersed silica can be used for preparing solid-phase reagents possessing anion-exchange properties. The sorption of (didecylaminoethyl)tridecylammmonium iodide (DDATD), *N*-methyl-*N,N,N',N',N'*-pentadecylethylenediammonium diiodide (PDEDA) and *N,N,N,N',N',N'*-hexadecylhexamethylenediammonium diiodide (HDHMDA) on silica gel Chemapol L 40/100 has been studied.^{88, 89} The maximum amount of DDATD adsorbed is 0.4 mmol g⁻¹, while those of PDEDA and HDHMDA are 0.12 mmol g⁻¹. It was proposed to use DDATD on silica gel for the concentration and determination of Co(II), Cu(II), Zn(II), Bi(III) and Mn(II) as acido-complexes.^{90, 91} This material is also suitable for the chemiluminescent and visual-test quantification of cobalt(II) in natural water (the detection limit is 2 mg litre⁻¹).

Visual tests for the analysis of cobalt and bismuth ions in drinking water at their contents close to the maximum permissible concentration have been developed.^{36, 91} The tests are based on the formation of coloured ion associates by bismuth tetrathiocyanocobaltate and bismuth tetraiodide on a silica gel surface. The sorption can be carried out in both static and dynamic regimes. Macro- and micro-components of natural water do not interfere with the determination.

The DDATD–silica gel system modified with chromophoric and luminescence reagents (indicators) of the anionic type: Methyl Orange, Methyl Red, picric acid and fluorescein, is also of interest.^{88, 89} In this case, ion associates of the composition DDATD:indicator = 1:1 are formed on the surface of the solid phase. Inorganic and low-molecular-weight organic anions do not displace the immobilised reagents from the surface. However, the indicators enter into exchange reactions with anionic surfactants and thus pass into solution. This provides the basis for a procedure for determining micro-quantities of sodium dodecyl sulfate in natural and waste waters. The indicator displaced to the solution from the sorbent surface is quantified by spectrophotometry or luminescence or by visual test methods.

To determine formaldehyde in air by high performance liquid chromatography, the air is pumped through a glass cartridge filled with silica gel impregnated with 2,4-dinitrophenylhydrazine.⁹² As a result, hydrazone is formed on the sorbent surface; then it is eluted with methanol and determined by UV spectroscopy at a wavelength of 365 nm.

b. Macrocyclic ligands

Sorption under dynamic conditions of Cd(II), Co(II), Mg(II), Ni(II), Pb(II) and Zn(II) ions on silica gel modified with macrocyclic ligands, diaza-18-crown-6, octaethylporphyrin and 8,9,17,18-dibenzo-1,7-dioxa-4,10,13,16-tetraazacyclooctadecane, has been studied.^{33, 69} At pH 6.7, Cd, Co and Mg are eluted from silica gel modified with diaza-18-crown-6 in the order Cd > Co > Mg, and at pH 4, Zn, Pb and Ni are eluted in the order Zn > Pb > Ni. In the case of modification by octaethylporphyrin and by 8,9,17,18-dibenzo-1,7-dioxa-4,10,13,16-tetraazacyclooctadecane, elution occurs in the order Mg > Co > Cd (pH 6.7) or Ni > Pb > Zn (pH 4). When two reagents are immobilised simultaneously on the silica gel, the sequences of retention of metal ions change: Co and Pb ions are eluted first.

Immobilisation of tetraphenylporphyrin and its complexes with Sn(IV), In(III) and Zn(II) on aminopropyl-silica gel (with a particle size of 10 µm) afforded sorbents for high performance liquid chromatography.⁹³ These sorbents ensure virtually complete chromatographic separation of the above metals in normal, reversed-phase and anion-exchange variants. Examples of anion-exchange separation of aromatic carboxylic acids and sulfonic acids have also been reported.

c. N,O-Reagents

8-Hydroxyquinoline (HQ) is among the most efficient extractants used for the determination of metal ions.⁹⁴ Since at present, there is a constant tendency to decrease the toxicity of the chemicals used in analytical procedures and the labour content of the procedures, it is no wonder that numerous studies devoted to the immobilisation of HQ on the surface of various sorbents and to their analytical applications have been published. Sorption of Al(III), Fe(III), Cd(II), Co(II), Cu(II) and Mg(II) from aqueous solutions by silica gel modified with HQ (HQ-SS) has been reported.⁹⁵ The kinetics of sorption of various metal ions are dissimilar. Thus at pH 6, quantitative sorption of Cu(II) is achieved over a period of 10 min, while Zn(II) is sorbed quantitatively over a period of 30 min. The HQ-SS sorbent is used to concentrate rare earth elements from natural waters and to separate them from barium.³¹ The possibility of using this sorbent for the extraction of traces of metals from sea water⁹⁶ has also been shown. The extracted metals were detected by various modifications of mass spectrometry,^{17, 25, 28, 32, 37} by atomic absorption spectroscopy in the on-line regime^{28, 37} and by inversion voltammetry.⁹⁷ HQ-SS is used successfully in the analysis of organic compounds, in particular, nitrophenol and chlorophenol present in water at levels higher than their maximum permissible concentrations.²⁹

To determine iron(III) ions in sea water in a flow regime, a sorbent based on HQ immobilised on the surface of a chelate resin has been proposed.⁹⁶ The iron ions were then desorbed and detected by the luminescence method.

It has been suggested to detect aluminium(III) and manganese(II) in the presence of iron(III) using C₁₆-silica gel modified with a mixture of octaethylporphyrin and 5-phenylazo-8-hydroxyquinoline taken in a ratio of 5 : 1.⁹⁸ The metal ions are quantified in the eluate by spectrophotometry in the presence of Xylylene Orange.

β -Hydroxynaphthylidene-*o*-aminophenol immobilised on the APA-8n anion-exchange resin has been used as a sensing element in an optical sensor for detecting Al(III) ions.⁹⁹ The chemical and analytical properties of this solid reagent and of the fluorescent complex with aluminium formed on the surface of the sorbent were studied. The advantages of using this solid reagent for the analysis of aluminium were shown.

The use of silica gel modified with 1-(2-pyridylazo)-2-naphthol (PAN) for the concentration and separation of Cu(II), Co(II) and Ni(II) ions, the contents of which in a solution are several mg per litre has been described.⁴⁰ The concentration factor exceeds 100. It has been shown²⁰ that copper(II) ions are sorbed at pH 5–7 under dynamic or static conditions with a concentration factor of 200. Copper(II) is determined after its desorption with a 0.1 M solution of thiourea or 0.03 M hydrochloric acid flowed at a rate of 0.3–0.4 cm³ min⁻¹. The presence of less than 0.1 mg of Cr(VI), 2 mg of Zn, 0.2 mg of Mn(II), 3 mg of Ca(II) and 3 mg of Mg(II) does not interfere with the determination of copper. The optimum conditions for the sorption of cobalt(II) ions with PAN–silica gel and for its subsequent quantification by diffuse reflection spectroscopy and by the visual test method have been established.³⁴

A linear colorimetric method for the determination of Fe(III) and Cu(II) using PAN–silica gel has been proposed.⁵⁷ One millilitre of a solution of a sample with pH 3.0 (Fe) or pH 2.5 (Cu) is injected with a syringe into a tube with modified silica gel. The quantity of the metal is found from the length of the coloured zone using a calibrating plot. Sorption of Pb(II) ions by the same sorbent was also studied.⁹⁹

Foamed polyurethane and ion-exchange resins modified with PAN are used for concentration of uranium(VI) prior to its determination by diffuse reflection spectroscopy.³⁵ It has been proposed to use an ion exchanger based on a copolymer of styrene with divinylbenzene modified with PAN to analyse river water for Cu(II), Zn(II), Fe(III), Cd(II), Ni(II) and Pd(II).⁵⁸

A procedure for the concentration of zirconium and its subsequent determination by spectrophotometry in the solid phase using the AB-17×8 sorbent modified by Eriochrome Black T (ECB T) has been developed.⁵⁹ The capacity of the sorbent with respect to zirconium under static conditions is 18.2 mg g⁻¹, and the detection limit is 9.6 mg litre⁻¹.

Silica gel treated with a mixture of ECB T with liquid anion-exchange reagent Aliquat 336 is capable of concentrating traces of transition and alkaline earth metals from water.⁹⁵ Neither alkali metal ions nor ammonium ions are sorbed on this anion exchanger. The sorbed metals are eluted with dilute perchloric acid and determined by atomic absorption spectroscopy. The modified sorbent makes it possible to concentrate these metals by a factor of 250. This served as the basis of a procedure developed for concentrating Fe(II), Cu(II), Pb(II), Ca(II) and Mg(II) ions from water and from solutions of sodium, potassium and ammonium salts by column chromatography.

An optical-fibre fluorescence sensor for simultaneous determination of Al(III) and Ga(III) or Al(III) and In(III) has been developed. The method involves the use of the Bio-Rad AG1-X4 anion-exchange resin modified with lumogallion.¹⁰⁰ The analysis is carried out in a dynamic regime. The minimum concentrations of Al, In and Ga that can be determined in this way are 0.02×10^{-6} , 3.0×10^{-6} and 0.2×10^{-6} mol litre⁻¹, respectively.

The optimum conditions for the sorption of U(VI) on the Silochrome C-120 silica gel with immobilised 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol were found.¹⁰¹ A new test form for the determination of uranium in the sorbate phase by diffuse reflection spectroscopy was proposed. The detection limit is 35 ng in a 10-ml sample.

Xylylene Orange (XO) immobilised on the surface of a polyacrylonitrile fibre filled with a finely dispersed anion-exchange resin has been proposed as the sensing element of an optical sensor for detection of Pb(II) and Th(IV) ions.⁸⁰ The response of the sensing element is formed over a period of 1–10 min at lead(II) and thorium(IV) concentrations of 1×10^{-8} – 3×10^{-6} mol litre⁻¹.

Discs of a fibrous material filled with a weakly basic anion exchanger with immobilised arsenazo I have been used to determine U(VI) ions.⁸¹ The discs with arsenazo I are suitable for rapid quantification of uranium(VI), which is sorbed in the dynamic regime and then determined by diffuse reflection spectroscopy. The detection limit for uranium is equal to 3×10^{-8} mol litre⁻¹. As in the majority of cases, the immobilised reagent increases the sensitivity and selectivity of the analysis. In addition, the use of this method extends the range of concentrations that can be determined relative to that in the method involving the formation of complexes with arsenazo I in aqueous solutions.

Cellulose materials have been modified with ethylenediaminetetraacetic acid and used to determine Cr(III), Fe(II) and Pb(II) ions by atomic absorption spectroscopy.¹⁰² The quantity of metal ions that pass from a solution to the surface of the sorbent depends on the duration of the contact between the phases and on the concentration of the metal in the solution. Lead ions are sorbed most efficiently.

Traces of vanadium(IV) and vanadium(V) in water are determined by atomic absorption spectroscopy after concentration and separation on columns filled with silica gel containing immobilised fluorinated β -diketones — benzoyltrifluoroacetone and thenoyltrifluoroacetone — and *N*-(2-aminoethyl)- γ -aminopropyltrimethoxysilane.²⁰ To determine the overall amount of vanadium(V) and (IV), a sample in an acetate buffer solution (pH 6) was passed at a rate of 10 cm³ min⁻¹ through a column filled with 1.5 g of modified silica gel. Then the sorbed material was eluted with 6 M hydrochloric acid, a $(1-10) \times 10^{-6}$ M solution of cobalt(II) serving as the internal standard. The separate determination of vanadium(V) and vanadium(IV) is based on the fact that they are sorbed differently at various pH. For the adsorption of V(V) ions, a solution with pH 3 was passed through a column with modified silica gel, and to extract V(IV) from the liquid phase, a

solution that had passed through the column was neutralised to pH 6 and then passed through a second column filled with the same sorbent. The detection limit for vanadium is $0.06 \mu\text{g litre}^{-1}$. Iron(III) and copper(II) ions as well as ions of other metals present in high concentrations can be masked by complexone III. This procedure was used to determine $1-2 \mu\text{g litre}^{-1}$ of vanadium in river water.

It has been shown that silica gel modified with reagents containing ethylenediamine and ethylenediaminetriacetate functional groups can be used for the separation and concentration of vanadium(V) and vanadium(IV).²² The separation is carried out using two columns filled with modified silica gel. The first column contains silica gel modified with a compound incorporating ethylenediamine functional groups, while the second column is filled with the sorbent modified with a compound with ethylenediaminetriacetate functional groups. At pH 2.5–3.0, only vanadium(V) is sorbed in the first column. When inductively coupled plasma atomic adsorption spectroscopy is used for quantification of vanadium(V), the detection limit amounts to 60 pg cm^{-3} .

The use of silica gel modified with zincon for concentrating Na, K, Mg, Ca, Al, Zn(II), Cd(II), Pb(II), Mo(II), Fe(III), Co(II), Ni(II) and Cr(III) ions from aqueous solutions of their salts at pH 1–9 has been proposed.¹⁰³ A procedure for the atomic-absorption determination of these ions was developed. Prior to the determination, the ions were eluted from the surface of the modified sorbent with solutions of hydrochloric or perchloric acid. Zincon is used both for the separation of these elements and for purification of solutions of some salts from Zn(II), Pb(II), Cd(II) and Cu(II) ions present as impurities.

A procedure for the anion-exchange concentration of Cu(II), Zn(II), Pb(II) and Cd(II) ions using an anion-exchange resin modified with sulfonate azo-dyes has been developed.¹⁰⁴

According to a known sorption-photometric method for the determination of palladium, the AB-17 $\times$ 8 anion exchange resin modified with nitroxaminazo (NOA) is used as the sorbent.¹⁰⁵ The limit of detection of microquantities of palladium is of the order of $10^{-4} \mu\text{g cm}^{-3}$.

A procedure for the on-line separation of Pb(II), Cu(II), Cd(II), Co(II), Zn(II), Ni(II) and Mn(II) ions has been developed.¹⁰⁶ The ions are sorbed on cartridges filled with sorbents based on silica gel ($40 \mu\text{m}$) with immobilised hydroxamic acid. The calibrating plots are linear over a wide range of concentrations ($0.01-5.0 \text{ mg litre}^{-1}$). The detection limits for Cu(II), Co(II), Zn(II) and Ni(II) ions are $5-10 \mu\text{g litre}^{-1}$, and those for Pb(II) and Cd(II) ions are 20 and $30 \mu\text{g litre}^{-1}$, respectively. This modified sorbent was used for analysis of tap water.

Sorbents based on ODS C18 silica gel or XAD-4 resin containing immobilised *p*-tert-butylcalyx[4]arenetetrahydroxamic acid have been used for the pre-concentration of traces of transition metal ions.¹⁵ The conditions for the sorption of Fe(III), Co(II), Pb(II), Cd(II), Mn(II), Ni(II), Zn(II) and Cu(II) ions in the pH range of 2–7 were studied. A procedure for chromatographic determination of copper(II), zinc(II) and manganese(II) in natural and other waters was elaborated.

d. S₃N- and S-containing reagents

A method for the spectrophotometric determination of micro-quantities of Ag(I) and Pd(II) in water involving the use of a poly(vinyl chloride) film modified with 4,4'-bis(dimethyl-amino)-thiobenzophenone has been proposed.⁶⁵ In aqueous solutions of metal salts, the colour of the modified films changes due to the formation of complexes on the solid surface. The intensity of the colour depends on the pH, duration of shaking, the temperature of the solution and the concentration of the metal. The largest factor of concentration (1000) is achieved under optimum conditions, namely, a 500-ml sample, a surface area of the modified film of 12 cm^2 , a shaking time of 60 min and a temperature of the solution under analysis of $40-60^\circ\text{C}$. The limit of detection of silver is $0.5 \mu\text{g litre}^{-1}$ and that of palladium is $0.2 \mu\text{g litre}^{-1}$.

A sensing element for the determination of Hg(II) has been produced by immobilisation of 4-phenylazo-3-aminorhodanine (PAAR) on discs of polyacrylonitrile fibre filled with finely dispersed KU-2 ion-exchange resin.⁸³ The colour of the complex with mercury develops over a period of 3–5 min (for an initial volume of 10 ml). The method makes it possible to determine mercury directly in a solution, the detection limit being $0.02 \mu\text{g cm}^{-3}$. Ions of many transition metals that usually accompany mercury do not interfere with its determination. The use of PAAR applied on the solid phase increases the selectivity of the analysis by an order of magnitude with respect to that achieved when mercury is determined using PAAR in solution.

A sorbent based on the AB-17 $\times$ 8 anion-exchange resin modified with 1-(2-thiazolylazo)-2-naphthol-3,6-disulfonic acid (TAN-3,6-S) has been proposed for the determination of copper.^{62,63} To extract micro-quantities of copper from aqueous solutions and from water–organic mixtures, sorbents with coverages of 43% and 8%, respectively, are used.¹⁰⁷ The sorption-photometric method for the determination of low concentrations of copper is more sensitive and selective than the known photometric method for the determination of copper with TAN-3,6-S in solution.

The optimum conditions for the absorption of Pd(II) by this sorbent were also elucidated.^{108,109} The amount sorbed depends on the nature and concentration of mineral acids as well as on the coverage of the sorbent with the modifier and on the presence of organic solvents. The detection limit for palladium(II) is $1.25 \mu\text{g cm}^{-3}$.

Sorption of Fe(III) ions on the AB-17 $\times$ 8 ion exchange resin in the chloride form modified with TAN-3,6-S has been studied.¹¹⁰ The formation of complexes of Fe(III) ions with TAN-3,6-S immobilised on the sorbent surface was studied by spectrophotometry. It was found that the ratios of the components in the complexes formed in solution and in the phase of the sorbent are identical.^{62,108}

Conditions for sorption of Ni(II) ions with this sorbent were studied over a wide pH range.⁶² The composition and the stability constant of the nickel complex formed in the resin phase were determined by spectrophotometry. The influence of the stoichiometry of the nickel complex with the modifying agent on the kinetic properties of the sorbent was considered.

Group concentration of Cu(II), Ni(II), Zn(II) and Cd(II) ions on the AB-17 $\times$ 8-Cl anion exchanger modified with TAN-3,6-S creates conditions for the subsequent X-ray fluorescence determination of these elements in the concentrate.^{111,112} A sorption-X-ray fluorescence procedure for the determination of micro-concentrations of these metals present simultaneously was developed. The detection limit is $0.35-1.2 \mu\text{g}$, and the concentration factor is 200.

The protolytic and optical properties of Silochrome C-120 with 4-(2-thiazolylazo)resorcinol immobilised on its surface have been studied. Chemical and analytical conditions for the interaction of this material with U(VI), Cu(II), Ni(II), Zn(II), Co(II), Pd(II) and Fe(II, III) ions were identified.⁶¹ The sorbent is used for the test determination of Co(II), Pd(II) and U(VI) ions present in concentrations of $0.005-0.03 \mu\text{g cm}^{-3}$ by diffuse reflection spectroscopy and also for determination of palladium and uranium in real objects.

The AB-17 $\times$ 8 anion-exchange in the chloride form modified with 2-(2-thiazolylazo)-5-diethylaminophenol (TADEAP) has been proposed as the sorbent for the determination of U(VI) present in a concentration of about $10^{-5}\%$ by solid-phase spectrophotometry.¹¹³ The analysis is carried out for alkaline solutions of complex compositions without preliminary separation of uranium from the accompanying elements.

A method for detecting traces of cadmium and copper in salt sediments of sodium chloride has been reported.²⁶ The method includes ion-exchange pre-concentration of the elements to be analysed on silica gel modified with a thiol and atomic absorption spectroscopy.

Reagents with xanthate and dithiocarbamate functional groups immobilised on a silica gel surface have been used to concentrate traces of noble metals.¹¹⁴ The Pd(II), Ag(I), and Pt(IV) ions are sorbed quantitatively on this material at pH 4–5 and 2–5. The ions are detected by the atomic absorption method after desorption.

e. O-Containing reagents

Silica gel modified with dodecylbenzenesulfonic acid has been used under dynamic conditions for ion-chromatographic separation of transition metal ions.¹¹⁵ Solutions of strontium salts containing citric, tartaric, oxalic, pyrophosphoric and dipicric acids added for complex formation were used as the eluents. The optimum conditions for the selective determination of Cu(II), Ni(II), Pb(II), Co(II), Cd(II), Fe(II) and Mn(II) cations were chosen. The analysis requires 25 min.

Eriochromocyanine immobilised on the XAD-2 support can serve as an optical sensor for the determination of Al(III).¹¹⁶ The content of this metal is found by diffuse reflection spectroscopy.

Extraction chromatography on columns filled with silica gel containing a mixture of high-molecular-weight and isomeric tertiary C₁₀ carboxylic acids 'Versatic 10' immobilised on its surface is used to separate indium(III) from accompanying elements.¹¹⁷ Indium(III) is sorbed quantitatively from acetate buffer solutions with pH 4.5–6.0 and is desorbed with solutions of mineral acids. Neither Fe(III), Ni(II), Co(II), Zn(II) and Cu(II) ions nor U(VI), Cr(III), Al(III), Tl(III), Ga(III), lanthanide, Zr(IV) and Th(IV) ions are sorbed under these conditions; they can be separated by choosing an appropriate mobile phase.¹¹⁷ The researchers cited presented examples of the separation of Al(III)–In(III)–Ga(III)–Th(III), UO₂(II)–In(III)–Zr(IV) and La(III)–In(III)–Th(IV) mixtures.

To analyse environmental objects, a procedure has been proposed in which traces of Cd(II), Cu(II), Mn(II), Zn(II) and Fe(III) are concentrated by sorption from aqueous solutions with pH > 6 on silica gel modified with 3-methyl-1-phenyl-4-stearoyl-5-pyrazolone (with a coverage of 4.2%).¹¹⁸ Desorption of metal ions is accomplished using 1 M hydrochloric acid, and the contents of metals in the eluate are determined by atomic absorption spectroscopy. This procedure was used to determine traces of Cu(II), Mn(II) and Zn(II) in tap water.

The analytical potentialities of morin immobilised on the KU-2 cation-exchange resin and on a dextran type sorbent, Sephadex G-25, have been studied.⁶⁰ These sorbents are suitable for selective determination of zirconium and tin in wastewater. The minimum concentration of Zr detected in this way is 1.0 µg cm⁻³ and that for Sn(II) is 0.5 µg cm⁻³.

f. Algae

Sorption of toxic metal ions (Co, Ni, Pb, Cd, etc.) from aqueous solutions by silica gel modified with an alga *Chlorella vulgaris* has been studied.⁵¹ The sorbent was used to concentrate metals, which were then quantified by atomic absorption spectroscopy.

A method for the immobilisation of marine algae cells on silica gel has been proposed.⁵² The material thus obtained was used to extract lead from aqueous solutions by column chromatography. The lead is determined after its desorption with a mixture of nitric and hydrochloric acids. The adsorption capacity of the modified sorbent with respect to lead decreases by 15% after 20 adsorption–elution cycles. This sorbent also extracts almost completely micro-quantities of cesium from strongly saline solutions.

2. Inorganic reagents

Methods for the preparation and applications of inorganic sorption materials based on various supports — carbon, zeolites, sand, wood cellulose, etc. — have been considered in a review.⁷¹ The accessibility of many of these supports, the ease of synthesis of sorbents based on oxides, hydroxides, ferrocyanides and other solid phases, their mechanical strength and high kinetic characteristics make these materials highly promising sorbents for process-

ing of natural and waste waters, liquid radioactive wastes and various solutions.

a. Metal salts

A separate group of sorbents comprises materials modified with inorganic salts; they are meant for the analysis of compounds capable of being involved in complex-formation, precipitation or redox reactions with the salts fixed on the surface.

Chromatographic behaviour of a large number of inorganic anions on silica gel modified with 0.1% aqueous solutions of CuSO₄, ZnSO₄, [Co(NH₃)₆]Cl₃ and NiCl₂ has been studied.⁴⁴ Desorption is carried out using water–organic mixtures containing mineral acids, and detection is accomplished using thin-layer chromatography and various visualising reagents.

A method for the separation of Tl(III) from Cd(II), Al(III), Ni(II), Fe(III), Ag(I) and Pb(II) using silica gel modified with sodium molybdate dissolved in a formic acid–butanol mixture has been reported.⁴³

A procedure has been proposed for the determination of aromatic sulfur-containing heterocyclic compounds in slate pitch. The method includes chromatography on columns filled with silica gel containing palladium(IV) chloride adsorbed on its surface.⁴² The analysis is performed by UV spectroscopy or flame photometry.

Sorption of cesium ions on silica gel with immobilised potassium tetracyanocuprate has been studied under static conditions.¹¹⁹ The rate of ion exchange between potassium and cesium increases as the capacity of the sorbent with respect to the above copper(I) complex decreases. The sorbent can also be used under dynamic conditions.

A method for preparing a sorbent based on iron(III) hexacyanoferrate(II) has been described.¹²⁰ Cellulose was treated with a mixture of solutions of potassium hexacyanoferrate(III) and iron(III) nitrate in a special mixing reactor. The capacity of the sorbent with respect to the modifying reagent was 300 to 600 mg cm⁻³.

Inorganic sorbents based on potassium hexacyanoferrate(III) have been obtained using precipitation reactions.¹²¹ The compositions and physicochemical and sorption properties of the materials depend on the conditions of their synthesis.

Oxidative and indicator systems based on modified silica gel have been used to determine nitrogen oxides in air.⁴⁶ The oxidative tube contained silica gel impregnated with an acid solution of potassium permanganate, while the indicator tube was filled with silica gel impregnated with potassium iodide, starch, sodium chloride and sodium thiosulfate.

Tin(IV), zinc(II) and aluminium(III) iodides applied on activated carbon are used to extract radioactive iodine from solutions.⁷¹

A number of sorbents based on potassium hexacyanoferrate(II) applied on a zeolite, an acrylic fibre or silica gel are used for treatment of radioactive wastewaters.⁷¹

Amorphous calcium phosphate applied on an acid-resistant porous support with an extensive surface is used as a sorbent for the concentration of heavy metal ions.

A sorbent possessing high selectivity with respect to strontium in calcium-containing solutions is prepared by treatment of coal with a solution of potassium permanganate containing 1.0 to 1.2 g litre⁻¹ of ammonia.⁷¹

b. Metal oxides and hydroxides

Oxide and hydroxide films immobilised on various inert matrices (sand, cellulose, activated carbon, various copolymers, etc.) constitute a large group of inorganic sorbents.

A sorbent based on manganese dioxide applied on a support is used for the sorption of Cu(II), Zn(II) and Pb(II) ions under dynamic conditions.⁷⁵

To purify water from iron, it is filtered through the so-called 'black sand',¹²² which is prepared by the successive treatment of sand with solutions of manganese chloride and potassium per-

Table 1. Chemical and analytical properties of analytical reagents.

Reagent	Sorbent	Capacity of the sorbent/ mmol g ⁻¹	Analyte	Optimal pH	Detection limit/ mg cm ⁻³	Method of determination ^a	Ref.
KU-2 cation exchanger + <i>p</i> -nitrosodiethylaniline	Polyacryl fibre (40–50 µm)	5.0	Pd(II)	2–3	5.3×10^{-4}	DRS	82
Lucigenin	Silpearl	0.034	V(IV)		0.7	CL	55, 66
	"	0.034	Fe(II)		0.8	CL	66
DDATD	Silica gel	0.24	Co(II)	200	0.002	CL	89, 90
Aza-analogue of dibenzo-18-crown-6	"	0.005	Co(II)	< 7	0.02	AAS	69
	"	0.005	Cu(II)	2–8	0.01	AAS	69
HQ	"		Lanthanides	8	$(3-5) \times 10^{-4}$	MS	31
	Hydrophilic vinylic polymer		Fe(III)	9.5	2.8×10^{-6}	CL	96
β-Hydroxynaphthalene- <i>o</i> -aminophenol	APA-8n	4.0	Al(III)	4.0–6.5	1.2×10^{-3}	CL	99
PAN	Silica gel		Co(II)	3–5	0.02–0.04	DRS	34
	Silochrome C-120		Cr(III)	2.5–4.5	0.1	DRS	39
	"		Mn(II)	5.0–7.5	0.05	DRS	39
	"		Fe(III)	5.0–6.5	0.3	DRS	39
	"		Ni(II)	6–9	0.03	DRS	39
	"		Cu(II)	5–8	0.1	DRS	39
	"		Zn(II)	7.5–10	0.03	DRS	39
KU-2 cation exchanger + PAN-2	Polyacrylic fibre (30–40 µm)	0.2	Cu(II)	5.7	0.032	DRS	79
ECB T	AB-17 × 8 (100–250 µm)	0.23 ^b	Zr(IV)	2	9.6×10^{-6}	SPSP	59
Lumogallion	Anion exchanger		Al(III) and Ga(III) or Al(III) and In(III)	3–8	5.4×10^{-4} 1.4×10^{-2} 5.4×10^{-4}	PL	100
Anion exchanger (5–10 µm) + XO	Polyacrylic fibre (30–40 µm)	0.06	Th(IV)		0.34 4.6×10^{-3}	DRS	80
Anion exchanger + arsenazo I	The same	0.03	Pb(II)		0.01	DRS	80
	"		U(VI)		7.1×10^{-4}	DRS	81
Zincon	"	0.1	Ca(II)	< 6			103
	"	0.1	Mg(II)	< 9			103
NOA	AB-17 × 8	2.5×10^{-3}	Pd(II)	6	$> 10^{-4}$	SPSP	105
TAN-3,6-S	AB-17 × 8 (100–250 µm)	1.6×10^{-3}	Ni	9	1.25	SPSP	62
	The same	0.016	Cu(II)	2		SPSP	107
	"	6.3×10^{-4}	Pd(II)	2.5–3.0	1.25	SPSP	108
	"	$> 1.6 \times 10^{-3}$	Fe(III)	3.8–4.3		SPSP	110
	"		Cu(II)	4–5		SPSP	112
TAR	Silica gel		Co(III)	4.0	0.005–0.3	DRS	61
	"		Co(II)	6.2	0.005–0.3		61
	"		Pd(II)	6.0	0.005–0.3	DRS	61
	"		U(VI)	7.4	0.005–0.3	DRS	61
TADEAP	AB-17 × 8-Cl	5.0×10^{-4}	U(VI)	6–9	$> 10^{-4}$	SPSP	113
Morin	KU-2 + Sephadex G-25	0.01–1.0	Sn(II)	0.2–1.3	0.5	CL	60
	"	0.01–1.0	Zr(IV)	0.3	1.0	CL	60
Algae	Silica gel	267 ± 6	Pd(II)	4.7		CC	52
PdCl ₂	"		Organic compounds			GC	42

^a DRS is diffuse reflection spectroscopy, CL is a chemiluminescence method, AAS is atomic absorption spectroscopy, MS is mass spectrometry, SPSP is solid-phase spectrophotometry, PL is photoluminescence, CC is column chromatography and GC is gas chromatography. ^b Capacity of the sorbent is expressed in mg g⁻¹.

manganate. This yields a sorbing layer of manganese dioxide. Sulfonated coal can be used instead of sand.

A flow injection procedure for the determination of organic reducing agents in water samples using lead(IV) oxide immobilised on a silica surface has been suggested.⁴⁵ The concentration of organic compounds in water is found from the quantity of Pb(II) resulting from the reaction of Pb(IV) with reducing reagents. The concentration of Pb(II) is determined by spectrophotometry using 4-(2-pyridylazo)resorcinol or by atomic absorption spectroscopy.

The sorbent obtained by precipitation of aluminium and iron(III) hydroxides from solutions of metal sulfates on activated carbon in the presence of coagulating agents based on polyacrylamide is also suitable for the extraction of heavy metal ions from water.⁷² The $\text{Al}(\text{OH})_3 : \text{Fe}(\text{OH})_3$: carbon ratio in this material is 1 : 4 : 5 by weight. The capacity of the sorbent with respect to uranium amounts to 266 mg g⁻¹.

Sorbents consisting of aluminium(III), iron(III) and manganese(II) hydroxides applied on copolymers of styrene with divinylbenzene with various degrees of cross-linking are used to concentrate microelements from sea water.¹²³ The factors of concentration of metals depend on the thickness of the hydroxide layer and on the degree of porosity of the support. The material is suitable for sorption under dynamic conditions.

The sorption on iron(III) hydroxide applied on various supports is used to purify solutions from water-soluble compounds of arsenic.^{71, 124} This procedure ensures extraction of traces of arsenic and arsenous acids, organic arsenic-containing acids and their derivatives.⁷¹

Composite sorbents prepared by deposition of titanium(IV) and zirconium(IV) hydroxides on the activated carbon BAU are selective with respect to phosphate and fluoride anions.^{73, 74} A sorbent of this type absorbs 2.4 times as much phosphate ions per gram as granulated titanium hydroxide, all other factors being the same. The high capacity of these materials with respect to phosphate ions is retained in neutral and weakly alkaline media.⁷¹

A sorbent consisting of a thin layer of iron oxide applied on sand has been proposed for the extraction of copper ions from washings containing ammonia.¹²⁵

To concentrate metal ions from sea water and industrial sewage, a sorbent has been proposed,¹²⁶ which consists of dispersed metal hydroxides, oxides or sulfides or of these compounds precipitated on or embedded into an organic or inorganic porous support (organic polymers, zeolites, molecular sieves). The synthesis of a sorbent based on zinc hydroxide and an organic support is described in the patent cited¹²⁶ as an example. Methods for preparing a composite sorbent for the extraction of heavy metal ions from sea water or wastewater have been developed.^{127, 128} This material is based on a porous support, for example, an organic polymeric gel in which finely dispersed aluminium, iron, manganese, titanium or other metal oxides and hydroxides are introduced. The quantity of the inorganic compound introduced is more than 0.1 mole per litre of the gel. The preparation of composite sorbents based on polyacrylamide and hydroxides of the above metals is described as an example. The exchange capacities of the sorbents with respect to copper(II), nickel(II), mercury(II), chromium(III) and some other heavy metal ions were determined. Characteristic features of the composite adsorbents are their high stabilities, good adsorption properties and easy separation from water.

A procedure for modification of inorganic sorbents consisting of hydroxides or insoluble salts of multi-charged metal ions applied on porous supports such as carbon, active sludge and sawdust has been reported.¹²⁸ These sorbents can be used to remove non-ferrous metal ions from wastewater of electrochemical plants.

Extraction of heavy metal ions from sea water can be carried out using adsorbents based on activated carbon, poly(vinyl acetate) or a fibrous non-woven material modified by treatment with a hydrosol of titanate acid (with a concentration of 5% – 10 % and a size of colloidal particles of 1 – 100 µm).⁷¹

The sorption properties and stability of titanium-containing sorbents on a sawdust support have been considered.^{129, 130} The kinetics of peptisation of a wood-supported titanium hydroxide layer in water were studied and some assumptions as to the nature of the bond between the sorption material and the support were made.¹³⁰

The main chemical and analytical characteristics of the immobilised reagents described above are summarised in the general Table 1.

V. Conclusion

Analysis of the published data indicates that the new line of research associated with the use in chemical analysis of reagents immobilised on the surface of various supports is quite promising. These reagents increase the sensitivity and selectivity of determination of many elements.

The decrease in the detection limits is achieved due to the concentration of the components to be analysed from a relatively large volume of a solution into the phase of a sorbent. Unlike extractive concentration, the sorption methods do not require the use of organic solvents and, hence, they cause no health hazard. The sorbents themselves are non-toxic and are readily separated from solutions by filtration, which makes the analysis quicker.

The better selectivity of these methods results from the fact that in some cases, owing to some geometrical features of fixing of organic reagents on a support surface, their complex-forming properties, for example, dentate number, change upon immobilisation. It can be assumed that modified sorbents extract most efficiently those metal ions that react with the immobilised reagent to give ion associates or complexes with a metal : ligand ratio of 1 : 1. In this case, steric restrictions caused by fixing of the ligand on the surface of the sorbent are minimised.

The subsequent development of this branch of analytical chemistry requires that the chemical nature of immobilisation of reagents on the surface of solid supports be elucidated.^{67, 131} At present, the reagents are mostly fixed on the surface of a matrix by ion – ion interaction; other types of interaction are used much more seldom. In the latter cases, the chemical nature of the interaction of reagents with the sorbent surface is usually ignored, and the way of immobilisation is selected empirically by changing the solvents. Study of the chemical nature of the interaction of various classes of reagents with the surfaces of supports and elucidation of the regularities of the complex-formation involving supported ligands would markedly extend the analytical potential of the sorption methods. It is also necessary to work out scientifically justified criteria that would permit 'solid-phase reagents' to be regarded either as organic reagents modified with a surface or as sorbents modified with analytical reagents; at the current stage of investigation, this consideration is sometimes difficult.

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The nature of electronic transitions in linear conjugated systems

A D Kachkovskii

Contents

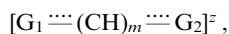
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Abstract. The current state of investigations of the relationship between electronic transitions and molecular topology of linear conjugated systems, *viz.* polymethine dyes and α,ω -disubstituted polyenes, is considered. The effect of parity of methine groups in a polymethine chain, of filling of the electronic shell, molecular symmetry, and the topology of terminal groups on the electronic structure of polymethines and polyenes are described. Spectral effects arising upon changes in the structures of chromophores, and the nature of the first and higher transitions in linear conjugated compounds containing several chromophores are discussed. The localisation of transitions in molecular fragments and the conditions for the inversion of the polymethine and local electronic transitions in polyenes and polymethines are considered. The bibliography includes 242 references.

I. Introduction

According to current theoretical concepts on the electronic structure of conjugated systems, in particular, the triad theory being developed by Daehne,^{1–4} the conjugated compounds with a stable closed electronic shell can be classed into three basic types: aromatic compounds, polymethines, and polyenes. Aromatic compounds have a cyclic structure, the CC bond lengths are equalised and the carbon atoms bear no noticeable charge. The linear conjugated systems (LCS) under consideration always have the *trans*-conformation. Polymethines are distinguished by the alternation of significant positive and negative charges on the carbon atoms and by maximum equalised CC bonds. On the contrary, polyenes are characterised by a significant alternation of the CC bond lengths and the lack of charges.

Linear conjugated systems contain, as a rule, terminal groups (TG) conjugated with the polymethine chain (PC). In the general case, LCS with a non-branched PC and one π -system can be represented as follows:



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where G_1 and G_2 are TG, m is the number of the methine groups, z is the charge ($z = 0; \pm 1; \pm 2$). Individual atoms, simple groups of atoms, and complex carbo- and heterocyclic residues with a branched π -system can serve as TG.

Traditionally, LCS with an odd number of polymethine groups in the PC are termed polymethine dyes (PMD); systems with an even number of π -centres in PC are termed α,ω -hetero-substituted polyenes or heterylpolyenes (HP).^{5–13} Symmetric PMD and HP differ substantially in several chemical and spectral properties, therefore, these two types of conjugated compounds are usually studied separately (it is especially true for experimental studies).^{6, 9, 14–16} If LCS have an asymmetric structure, the difference between PMD and HP decreases.

Linear conjugated systems are suitable and favourite objects for the studies of problems of the colour theory. A chromophore in these systems has a relatively simple structure that can be easily varied; their absorption and fluorescence spectra manifest relatively narrow and intense bands, especially in the case of PMD. It permits a reliable identification of electronic transitions and successful application of methods of quantum chemistry to studies of the relationship between structure and colour.

Due to unique spectral characteristics of LCS, they have found widespread practical application connected with the transformation of light energy. For example, LCS are used as optical sensitizers,^{13, 17–19} active media and passive modulators of the duration of lasers,^{20–24} initiators for polymerisation reactions,^{25–28} organic photoconductive materials,^{29–32} systems with a high polarisability for non-linear optics,^{33–37} and fluorescent markers.^{33, 39}

The creation of novel promising compounds with a given range of absorption and a number of other properties usually presumes preliminary estimation of the most important of their characteristics. This estimation is based on the well-developed colour theory or more precisely, on the theory of electronic transitions. The present review is devoted to the consideration of the current status of investigations of the relationship between molecular topology of LCS and the nature of their electronic transitions.

II. Specific features of electronic structure

1. Boundary molecular orbitals and classification of linear conjugated systems

Boundary molecular orbitals (BMO), *viz.*, the highest occupied (HOMO), and the lowest unoccupied (LUMO) orbitals, and the

orbitals close to them in energy are the most interesting for the theory of electronic transitions in LCS.

Symmetrical LCS (see 1, where $G_1 = G_2 = \text{TG}$) can be subdivided into four groups according to the symmetry of BMO and the parity of the number of the methine groups in PC.⁴⁰

1. Polymethines of class A in which m is odd, the HOMO is symmetric, and the LUMO is antisymmetric relative to the central atom;

2. Polymethines of class B in which m is odd, the HOMO is antisymmetric, and the LUMO is symmetric relative to the central atom;

3. Polyenes of class A in which m is even, the HOMO is symmetric, and the LUMO is antisymmetric relative to the midpoint of the central bond;

4. Polyenes of class B in which m is even, and the symmetry of the HOMO and LUMO is opposite to that of LCS of group 3.

Lengthening of the chain of PMD or HP by one vinylene group is accompanied by a change in the class of the compound. The class of LCS depends also on the number of the HOMO: the addition or removal of a pair of π -electrons changes the class to the opposite one.

The linear conjugated systems can exist in several forms depending on the ratio between the number of π -electrons and p-centres. Thus for non-substituted polymethines or PMD with alternant hydrocarbons as the TG, two forms are possible, namely, the electron-excess or $(N + 1)$ form (polymethine cation) and the electron-deficient or $(N - 1)$ form (polymethine anion), where N is the number of π -centres. In the case of non-substituted polyenes or HP with alternant TG, three forms are possible: the electron-excess $(N + 2)$ form, the electron-balanced N -form, and the electron-deficient $(N - 2)$ -form.⁴¹

2. Electron donor ability and topological indices of terminal groups

In the Hückel approximation, occupied and vacant levels in unsubstituted polyenes are symmetric relative to the level of the non-bonded π -electron (the Fermi level of π -electrons), whereas non-substituted polymethines contain a non-bonding level that is occupied in anions and vacant in cations. The distance between the Fermi level and neighbouring levels decreases with a lengthening of PC, however, the relative position of the energy gap between the highest occupied and the lowest vacant levels remains the same. The introduction of a TG results, as a rule, in the change in the relative position of the energy gap in LCS.

A φ_0 parameter was proposed⁴⁰ for quantitative characterisation of the relative position of boundary levels

$$\varphi_0 = 90^\circ \frac{\varepsilon_e - \alpha}{\varepsilon_e - \varepsilon_0}, \quad (1)$$

where ε_e is the energy of the LUMO, ε_0 is the energy of the HOMO, and α is the energy of the Fermi level.

Another form of the representation of the φ_0 parameter is

$$\varphi_0 = 90^\circ \frac{x_i}{x_e - x_0},$$

where x_i is the energy of an i th MO expressed in the β units and referred to the Fermi level α , $x_i = (\varepsilon_i - \alpha)/\beta$; ε_i is the energy of any i th MO, and β is the resonance integral of the CC bond in PC.

It is seen from formula (1) that an increase in the φ_0 parameter should correspond to an increase in the polarographic reduction potential and the electron affinity and to a decrease in potentials of oxidation and ionisation. The φ_0 parameter reflects the electron donating properties of LCS and is therefore termed as the electron donor ability.⁴⁰

For molecules with stable, closed electronic shell, the φ_0 value is usually positive and falls within the interval

$$0 \leq \varphi_0 \leq 90^\circ. \quad (2)$$

A model of LCS with a rather long PC appeared to be useful for a quantitative account of the influence of the topology of TG.^{12,42–46} In the context of this model, the energies of the boundary and close molecular orbitals (ε_l) can be represented as a function of parameters of individual molecular fragments.

$$\varepsilon_l = \alpha + \frac{2(\Phi_{01} + \Phi_{02} - \pi l/2)}{m + L_1 + L_2} \beta, \quad (3)$$

where m is the number of methine groups in PC, Φ_{01} , Φ_{02} , L_1 , and L_2 are topological indices of both TG, l is the number of the MO.

The topological parameter of the zero order Φ_0 corresponds to a displacement of the nodes of BMOs from the positions that they occupy in non-substituted LCS. This parameter characterises the ability of TG to donate the π -electron density to the atoms of PC.⁴⁷ It can be compared with the value of additional stabilisation of double bonds (ASDB)⁴⁸ introduced by Brooker and with experimental estimations of the properties of TG as bases, for instance, with the parameter b ('basicity') proposed by Platt⁴⁹ or 'electron donor ability' D proposed by Il'chenko.⁵⁰

The topological index L reflects quantitatively the effective lengthening of a chromophore at the expense of the π -system of TG and can be expressed by the equivalent number of methine and vinylene groups.

The parameters Φ_0 and L are calculated *via* junior coefficients of the polynomial for TG ($Q = q_0 + q_1x + \dots$) and its minor ($R = r_0 + rx_1 + \dots$) with no regard to the atom bound to the PC.^{44,46}

$$\text{tg } \Phi_0 = -\frac{q_0}{r_0}, \quad (4)$$

$$L = \frac{2q_1r_0 - 2q_0r_1 + q_0^2}{q_0^2 + r_0^2}. \quad (5)$$

In the framework of the model of long LCS, the additive parameters of TG of higher order were also obtained,^{51–53} however, only two topological indices Φ_0 and L are used in practice.

It was shown⁴⁰ that the topological parameter of the zero order Φ_0 is directly connected with the electron donor ability φ_0 by the following relations:

for PMD

$$\Phi_0 = \lim_{m \rightarrow \infty} \varphi_0, \quad (6)$$

for HP

$$\Phi_0 = \lim_{m \rightarrow \infty} \varphi_0 \pm 45^\circ. \quad (7)$$

The sign in formula (7) depends on the form in which the HP exists.

The parameter φ_0 characterises the relative position of the boundary levels, *i.e.* it has a distinct physical meaning and can therefore be measured experimentally. For example, linear relationships between redox potentials, the transition energy, or the ionisation potential, on the one hand and calculated energies of MO, on the other hand, can be used for this purpose.⁵⁴

The parameters φ_0 and Φ_0 appeared to be useful for the analysis of the relative stability of LCS, which is understood as the stability of π -systems with the same values of the energy gap, *i.e.* of those absorbing in the same spectral range.⁴¹ The π -system is supposed to be stable if all the bonding levels are mutually filled and antibonding levels are vacant; in this case condition (2) is fulfilled. Molecules with a medium electron donor ability ($\varphi_0 = 45^\circ$) in which the energy gap is symmetrical relative to the Fermi level, appear to be the most stable.

According to formula (1), a change in the number of the HOMO by a unity, *i.e.* the passage from one group of LCS to another, corresponds to a change in the parameter φ_0 by 90° .

Hence, with regard to condition (2), only one form should be stable within the limits of the model with equivalent bonds. In fact, symmetric PMD that are characterised by equalising of bond lengths in PC exist, as a rule, in one form. Non-substituted polymethines or PMD with alternant TG having the boundary values of the φ_0 and Φ_0 parameters are the exceptions, when two unstable forms are possible.^{5, 7–12} It is seen from the ratio (6) that the maximum relative stability of PMD is ensured by TG with medium electron donor ability (with $\Phi_0 = 45^\circ$).

In the case of HP, the essential alternation of bond lengths in PC leads to an additional increase in the energy gap, larger displacement being experienced by the boundary level that is located closer to the Fermi level.⁴¹ The relationship between the φ_0 and Φ_0 parameters [see formula (7)] is complicated due to the alternation of bonds, therefore the electron donor ability changes less ($\Delta\varphi < 90^\circ$) on going from one form to another. Thus in the case of polyenes two forms are stable, as a rule (see, for example, a review⁶). Polyenes containing TG with the limiting values of the index Φ_0 equal to 0 or 90° appear to be the most stable. In this case, even three forms are able to exist: a stable, electron equalised and two less stable, an electron excess and electron deficient ones.⁴¹

3. Distribution of the electron density on atoms and bonds

a. Atomic charges

Non-substituted polymethines with a closed electronic shell are charged. The values of charges on the carbon atoms are defined as squares of coefficients of non-bonding MO (NBMO). The NBMO has nodes in the even positions. The nodal atoms bear no charges. In the odd positions, the charge value Δz depends on the number of π -centres in the chain (N), and the sign depends on the form of polymethine.

$$\Delta z \simeq \pm \frac{1}{N+1}. \quad (8)$$

The introduction of a TG is accompanied by a change in absolute values of charges in the odd positions and by induction of charges in the even positions. Formulae of the perturbation theory⁵⁵ can be used for the analysis of changes in the π -electron density q_μ .

$$q_\mu = q_\mu^0 + \pi_{1,\mu} h, \quad (9)$$

where q_μ^0 is the electron density on the μ th atom in non-substituted LCS, $\pi_{1,\mu}$ is atom-atomic polarisability, h is the magnitude of perturbation on the terminal atom of the chain.

For the middle of the chain we have

$$\pi_{1,\mu} \simeq \frac{1}{N+1} \left[\frac{2}{\pi} + (-1)^\mu \right] \text{ at } \mu \rightarrow \frac{N}{2} \text{ or } \frac{N+1}{2}. \quad (10)$$

It follows from formulae (9) and (10) that the sign of a change in the electron density depends on the sign of the term $(-1)^\mu$, i.e. on the parity of the position of TG. Consequently, the effects of TG in neighbouring positions are inverse. If a molecule of PMD contains two TG, their influence is synchronous because the parities of any position relative to both ends of the chain coincide.

According to the rule of 'topological charge stabilisation',^{56–58} the significant alternation of the electron density on atoms causes the relatively high stability of odd conjugated systems. *ab initio* Calculations have shown that polymethines are stabilised largely at the expense of a lowering of the potential energy of the π -electrons, while aromatic systems are stabilised due to their low kinetic energy.^{57, 58}

Hückel, PPP, CNDO/2, and MINDO/3 calculations have shown that the ratio between the absolute values of positive and negative charges on the carbon atoms in neighbouring positions in PMD depends unambiguously on the topological index Φ_0 (Fig. 1).^{12, 59–61}

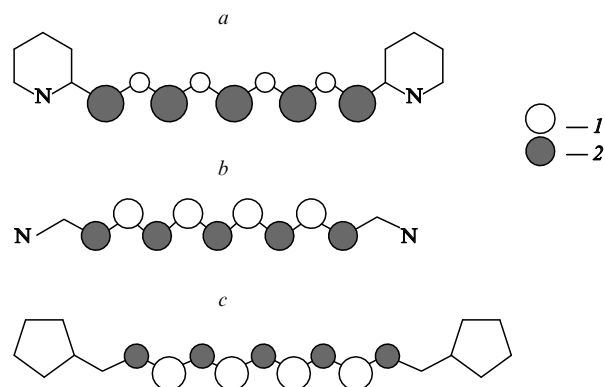


Figure 1. Charges on atoms of PC in the ground state. Charge: (1) is positive, (2) is negative. Φ_0 /grad: (a) 76, (b) 45, (c) 27.

In contrast to polymethines, the π -electron density in non-substituted polyenes in the stable *N*-form, is uniformly distributed over all the carbon atoms, and the π -charges are lacking. The introduction of one TG induces the alternation of positive and negative charges as in the case for polymethines with one TG. However, in the case of symmetrical HP, the overall influence of two TG differs from that for symmetrical PMD, since for polyenes the parities of any position of carbon atoms in the chain relative to each end are opposite. This results in the annihilation of alternating charges in the middle of the chain in symmetrical HP.^{60, 61}

The regularities found for the charge distribution in the ground state of PMD and HP are confirmed by experimental observations, in particular, of the changes in chemical shifts in ^{13}C NMR spectra as the molecular topology of LCS varies.^{5, 62–66, 69}

A change in the π -electron density on going to the excited state Δq_v can be written in the analytical form:^{12, 60, 61} for PMD

$$\Delta q_v = a(-1)^{n+v+1} \cos\left(v\frac{\pi}{2}\right) \cos\left[va\left(\frac{\pi}{2} - \Phi_0\right)\right], \quad (11)$$

for HP

$$\Delta q_v = a(-1)^{n+v} \sin\left(v\frac{\pi}{2}\right) \cos\left[va\left(\frac{\pi}{2} - \Phi_0\right)\right], \quad (12)$$

where $a = 1/(n+L)$, n is the number of vinylenes groups in PC, v is the number of the atom counted from the midpoint of PC.

Changes in populations on neighbouring atoms are opposite in sign due to the first multiplier which is confirmed by calculations using more rigorous approximations.^{56–61}

An analysis of formulae (8)–(12) and of the results of quantum-chemical calculations shows that the excitation of the atoms of PC in symmetrical PMD results in recharge, i.e. the signs of the charges in the ground and excited states are opposite. In the case of symmetrical polyenes, the signs of the charges remain the same upon the transition of the molecule to the excited state.

b. Bond orders

The π -electron density on atoms of PC in PMD alternates strongly, whereas in HP it is equalised. As far as populations of bonds are concerned, the situation is opposite: populations alternate in polyenes and equalise in polymethines.^{1–4}

Calculations of symmetrical PMD predict nevertheless some alternation of the CC bond orders if the topological index Φ_0 (and therefore the electron donor ability φ_0) has an increased or decreased value; the amplitude of alternation is minimum in the midpoint of the chain and increases towards its ends.^{61, 67} Not

only the p_{uv} value of bond populations, but also the order of sequence of the bonds with larger or lesser population change with the change in the parameter Φ_0 . The absolute value of p_{uv} depends on the extent to which the parameter Φ_0 differs from the average value of 45° .

Non-equivalence of the CC bonds in PC of symmetrical PMD is confirmed by X-ray spectroscopy^{68,69} and by direct coupling constants in the NMR spectra.^{70–72}

Using analytic expressions for coefficients of MOs and, respectively, for bond orders in unsubstituted LCS,^{55,73–75} the amplitude[†] of the alternation of bonds can be calculated.

$$\Delta_\mu = p_{\mu,\mu+1} - p_{\mu+1,\mu+2}.$$

It has been shown that at the beginning of the chain of rather long polymethines and polyenes, the Δ_μ value approaches to the same limiting value of $1/\pi$, however, in the middle of the chain, the amplitude of the alternation of bonds differs significantly for different types of LCS: for PMD

$$\Delta_\mu \simeq \frac{(-1)^{\mu+1}}{(N+1)^2}; \quad (13)$$

for HP

$$\Delta_\mu \simeq \frac{(-1)^{\mu+1}}{N+1}. \quad (14)$$

Significant alternation of orders and, respectively, of bond lengths in polyenes is predicted by calculations within the more rigorous, *viz.*, semiempirical^{15,16} and *ab initio*,¹⁵ approximations. In the majority of cases, the difference between the lengths of neighbouring bonds is close to 0.08 Å. The degree of the alternation changes little upon introduction of donor and acceptor substituents.^{76–80}

On going from one form of polyenes to another, the order of sequence of the bonds with larger or lesser population, *i.e.* the sign of the parameter Δ_μ changes to the opposite. In the excited state, the alternation of bond orders decreases though for polyenes and the difference in the orders of neighbouring bonds still remains significantly larger than that for polymethines, the order of sequence of the bonds with increased and decreased population being opposite to that in the ground state.

c. Ideal electronic states

Daehne^{1–4} has introduced the concepts of ideal polymethine and ideal polyene states. In the general case, for LCS with an arbitrary TG, the conditions for the realisation of the ideal electronic states can be pointed out using the electron donor ability φ_0 and topological indices of the TG.^{40,61} Thus the ideal polymethine state is achieved in symmetrical PMD with the TG for which $\Phi_0 = 45^\circ$. In this case, $\varphi_0 = 45^\circ$ and the boundary levels are located symmetrically relative to the Fermi level, bond orders are equalised in both the ground and excited states, and the charges alternate to the maximum extent. The excitation of ideal polymethines leads to the maximum change in the electron density and to the minimum change in bond orders.

The opposite situation in the distribution of the π -electron density corresponds to the ideal state of polyenes in symmetrical HP. The boundary levels are also located symmetrically and $\varphi_0 = 45^\circ$, however, it is provided by the terminal residues with $\Phi_0 = 0$. The charges on the atoms in the ground and excited states are absent, but the difference in populations of neighbouring bonds is a maximum; the change in bond orders in the excitation is also a maximum.

Hence, both ideal states are achieved at $\varphi_0 = 45^\circ$, however, ideal polymethines contain a TG with $\Phi_0 = 45^\circ$ and ideal polyenes contain a TG with $\Phi_0 = 0^\circ$.

d. Asymmetric LCS

The violation of symmetry in molecules of LCS leads to the shift of nodes of MOs towards one TG. It is convenient to characterise the degree of asymmetry by the difference in the topological indices of the terminal residues

$$\Delta\Phi_{12} = \Phi_{01} - \Phi_{02},$$

the numbers of TG are denoted by subscripts 1 and 2.

It follows from calculations of asymmetrical PMD that the charges decrease in the middle of PC as the parameter $\Delta\Phi_{12}$ increases (see Ref. 47). At the ends of the chain of asymmetrical PMD, 'the behaviour' of charges is determined by the nature of the neighbouring TG, and the effect of the second TG decreases inversely with the length of PC.

Bond orders in asymmetrical PMD depend on two major factors, namely, the difference in the topological indices of the terminal groups $\Delta\Phi_{12}$ and the electron donor ability, which is connected with the topological indices by the relationship

$$\varphi_0 = \frac{\Phi_{01} + \Phi_{02}}{2}.$$

The latter factor causes an alternation of bonds from the centre of PC to its ends, as in symmetrical polymethines, which is proportional to the absolute value of the difference $|45^\circ - \varphi_0|$. The maximum alternation, uniform along all the chain, is achieved if $\Phi_{01} > 45^\circ$ and $\Phi_{02} < 45^\circ$.

In contrast to polymethines, the violation of symmetry in HP leads to an increase in the alternation of charges on neighbouring atoms and to a decrease in the alternation of bond orders in proportion to $\Delta\Phi_{12}$.

It was found that in the excited state the amplitude of the alternation of bond orders in asymmetrical PMD and HP is substantially less than that in the ground state.⁴⁷ Note that in solutions the polarity of a medium can also influence the degree of alternation of bonds.⁷²

III. Topology of polymethine chromophore

1. Electronic levels and transitions

The colour of LCS is known^{1–3} to be determined by intense $\pi \rightarrow \pi^*$ electronic transitions. The intensity of possible $n \rightarrow \pi^*$ transitions is negligibly small, therefore, they will not be considered in the present paper.

In non-substituted conjugated molecules, the π -orbitals are completely delocalised. However, if LCS contain complex TG with a developed π -system, orbitals localised largely on the terminal residues can appear. For the sake of convenience, the orbitals delocalised over all the molecule were suggested to be termed as polymethine MOs and those localised mainly in TG local or more precisely, quasi-local MOs.^{81–83}

Thus, in the general case, two major types of $\pi \rightarrow \pi^*$ transitions are possible in LCS, *viz.*, transitions between the polymethine MO (levels), the so-called polymethine electronic transitions (PET) and transitions with the participation of local levels, *i.e.* quasi-local and local transitions (LET).

Polymethine and local electronic transitions differ substantially in several characteristics: in the value of dipole moment, in the sensitivity to the length of PC and topology of TG, to the effect of substituents. As a rule, LET is accompanied by a significant intramolecular charge transfer from one fragment to another in which the MOs that take part in the given transition are localised.^{39,82,83} In this case, the dipole moment of the molecule increases strongly, these transitions are therefore sensitive to the polarity of a solvent.^{82–85} The corresponding absorption bands differ also in intensity and contour.⁸¹

[†] The difference between two values for neighbouring atoms or bonds and for two states, the ground and excited one, is denoted as amplitude.

Calculations show that in symmetrical PMD with equalised bonds, electronic levels in the vicinity of the Fermi level are arranged uniformly, and the first excited state is mainly described by the χ_1 configuration (Fig. 2). If the function of the p th excited state Ψ_p^* is represented as the expansion within the basis of χ_i electronic configurations

$$\Psi_p^* = \sum_i T_{ip} \chi_i,$$

it turns out that $T_{pp} > 0.9$. This allows the use of a one-configurational approximation often to a sufficient accuracy.^{5, 7, 12, 47, 61, 67}

Since the boundary MOs of symmetrical LCS have opposite symmetries, the first transition is antisymmetrical, $A_1 \rightarrow B_1$ and the moment μ_1 is directed along the polymethine chain. The next two transitions are symmetrical and are described by a superposition of χ_2 and χ_3 configurations (Fig. 2a); their moments are polarised perpendicular to PC. In the approximation of long LCS, the χ_2 and χ_3 configurations have the same energies E_2^0 equal to double the energy of the χ_1 configuration (Fig. 2b). The interaction of the configurations leads to two excited states with energies

$$E^+ = E_2^0 + h$$

and

$$E^- = E_2^0 - h,$$

where $h = \langle \chi_2 | \hat{H} | \chi_3 \rangle$ is the interaction energy, $|\hat{H}|$ is the Hamiltonian.

In the case of PMD, the splitting value h is relatively small and the energies of the second and the third electronic transitions exceed significantly the energy of the first PET (see Fig. 2b).

For polyenes, the distance between the boundary levels increases due to the alternation of bond lengths, whereas the

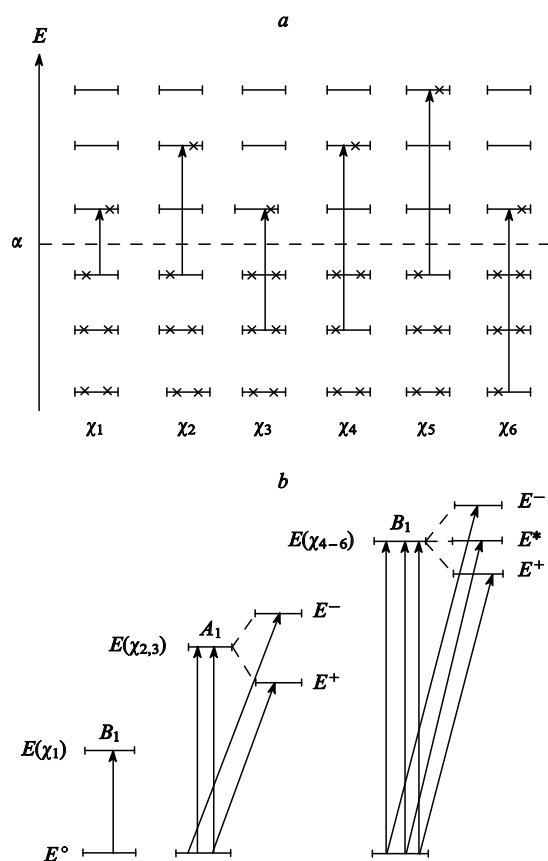


Figure 2. Electronic levels, single-excited configurations χ_i (a), and electronic states and transitions (b) in polymethines.

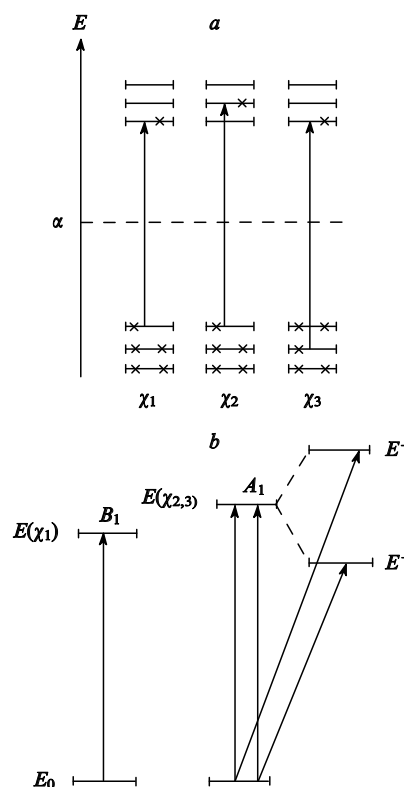


Figure 3. Electronic levels, single-excited configurations χ_i (a), and electronic states and transitions (b) in polyenes.

next vacant and occupied levels are located closer to the corresponding boundary level (Fig. 3); at a sufficient lengthening of the chain, the levels form zones.^{15, 16, 86, 87} As a consequence, the energy of the transition between the boundary levels ($A_1 \rightarrow B_1$) is always larger for polyenes than that for polymethines containing even shorter PC (see Fig. 3), which is confirmed experimentally (for instance, a large body of spectral data are reported⁸⁸ for PMD and HP).

In polyenes, the energies of χ_2 and χ_3 configurations differ from that of χ_1 configuration significantly less than in polymethines (see Fig. 3a). If the distance within the zones is relatively small and the interaction of the configurations is significant, the energy of one of the split states of the A_1 symmetry can appear to be even lower than that of the antisymmetrical B_1 state (see Fig. 3b).^{15, 16, 89–100} The symmetry forbidden A_1 state was really found experimentally (by two-photon spectroscopy) in non-substituted polyenes as the state with the lowest energy.^{15, 93, 101} Note that the excitation of polyenes is accompanied by equalising of the bonds; it can lead to the inversion of excited states of different symmetries. Thus in α,ω -diphenylbutadiene, photoemission occurs from the B_u state whereas absorption corresponds to the transition to the A_g state.¹⁰² In longer polyenes, the A_g state is emitting.

The introduction of a TG and the transition of one form to another lead, as a rule, to an increase in the distance between the levels within the zones and, therefore, to an increase in the difference between the energies of the χ_1 and the higher χ_2 and χ_3 configurations. That is why in these polyenes, the lowest excited state is still described by the χ_1 antisymmetrical configuration; it is the $A_1 \rightarrow B_1$ transition having a larger moment that is responsible for the colour of HP.

2. The length of polymethine chain

Koenig¹⁰³ has discovered experimentally that the lengthening of PC in symmetrical PMD shifts regularly the maximum of the absorption band to the long wavelength range. The value of this

shift upon the introduction of one vinylene group was termed as the vinylene shift

$$V = \lambda_{n+1} - \lambda_n,$$

the V value appeared to remain approximately constant in vinyl-ogous series of PMD and is equal to ~ 100 nm.^{5, 48, 49, 88, 104} Therefore, the vinylene shift can be considered as an additive contribution of one vinylene group (topological unit of PC) to this integral characteristic of the molecule as the absorption wavelength λ_n .

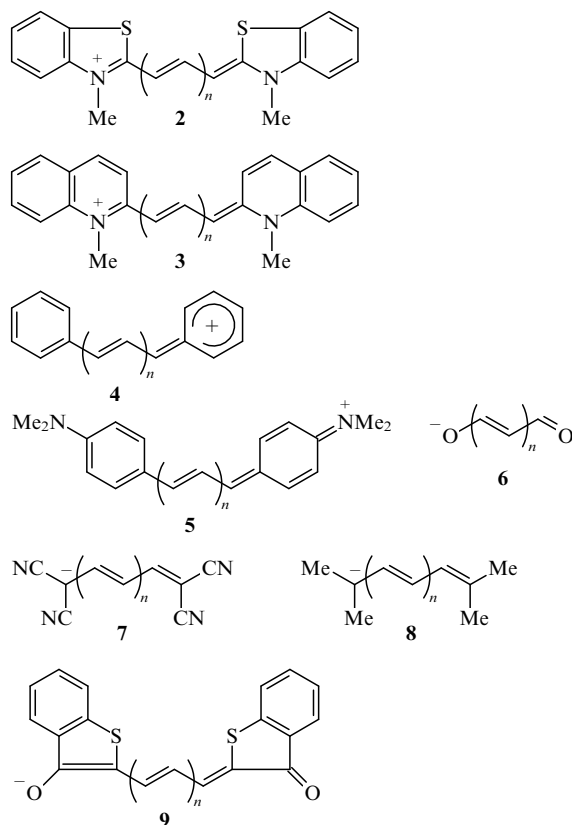
In vinylogous series of HP and asymmetrical PMD, the vinylene shift decreases regularly; Brooker called these series convergent unlike non-convergent series in the case of symmetrical PMD with a constant vinylene shift.⁴⁸

Naturally, similar shifts of the bands with the lengthening of PC is also observed in fluorescence spectra. It was shown that the V values in the fluorescence and absorption spectra of symmetrical PMD are nearly the same.^{12, 23, 24, 105–107}

PPP and CNDO/C calculations of the vinylene shift for vinylogous series of LCS show that the value of the parameter V depends, first, on the degree of equalisation of bonds in PC; alternation of bonds leads to an increase in the energy of PET in proportion to the number of bonds thus resulting in a decrease in vinylene shifts.^{5, 12, 104} It was shown above that bond orders in PC are 'sensitive' to the electron donor ability ϕ_0 , the type and shape of LCS, symmetry, and topological indices of TG. These factors should also influence the additive contribution of PC into the wavelength of PET.

a. Vinylogous series of polymethine dyes

Since PMD are characterised by equalising of bonds, significant vinylene shifts are observed in their spectra that change little with the lengthening of PC. Figure 4 shows the spectral data for the following vinylogous series of the most known polymethines:



The vinylene shift changes somewhat with the change in the polarity of a solvent.^{85, 108, 109}

In some species of PMD, the first vinylene shift deviates from an average value of 100 nm due to the interaction between TG in

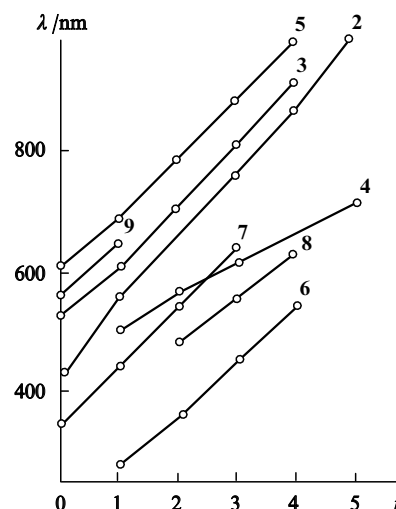


Figure 4. The dependence of wavelengths of the maxima of absorption bands $\lambda_{\max}$ of PMD 2–9 on the chain length.

monomethine dyes ($n = 0$), which disappears as the PC lengthens. Thus for quino-2-monomethinecyanines 3, ($n = 0$), steric hindrances are accompanied by a bathochromic effect and V is equal to 82 nm, whereas the second and the third vinylene shifts are equal to 98 and 100 nm.¹⁰⁴ In the case of dyes 2 and 9, the V value is influenced by the resonance interaction of valent non-bonded sulfur atoms, and the spectral effect depends on the class of compound: if the monomethine dye belongs to class A (2), the first vinylene shift is increased ($V = 182$ nm); if the first member of the series belongs to class B (9, $n = 0$), the V parameter decreases and is equal to 65 nm.¹¹⁰

The vinylene shift is 'sensitive' to the topology of TG.^{104, 111–113} If the Φ_0 index differs significantly from the average value of 45° , as, for example, in PMD 4 ($\Phi_0 = 0^\circ$), the alternation of bonds from the centre to the ends appears in PC and the value of the V parameter decreases to 60 nm.¹⁰⁴

b. Vinylogous series of heterylpolyenes

For polyenes, the dependence of the energy of PET on the PC length and the Φ_0 topological index is even more complicated due to both significant bond alternation and the possibility for the existence of several stable forms. It should be also noticed that the absorption bands for HP are relatively broad, their maxima are poorly resolved (see, for example, Refs 114–117).

The fact that the difference in the lengths of neighbouring bonds is a maximum in non-substituted polyenes causes very small vinylene shifts and their gradual damping as the PC length increases.^{15, 88, 104} An increase in Φ_0 with the introduction of TG is accompanied by some increase in the parameter V . Thus for non-substituted polyenes $V = 33–18$ nm at $n = 1–6$, for conjugated α,ω -diketones ($\Phi_0 = 63^\circ$) $V = 50; 50; 33; 29; 26$ nm at $n = 1–6$.¹¹⁸

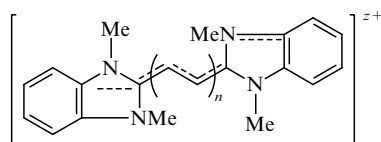
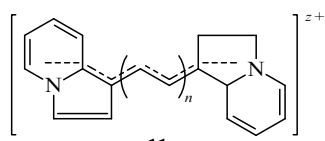
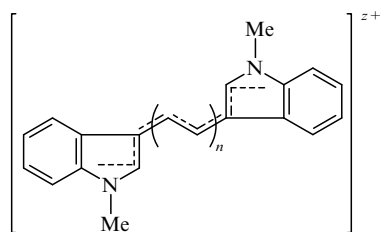
The amplitude of alternation of bond lengths depends also on the shape of a polyene which should also influence the magnitude of the vinylene shift. Thus, for the electron-equalised N -form of α,ω -diphenylpolyenes, $V = 28–17$ nm at $n = 1–6$; for the electron-excess ($N + 2$) form, $V = 50$ and 57 nm at $n = 4; 5; 6$.^{88, 104}

It appeared that in the cases when two forms of HP are possible, the more stable form as a system with a larger amplitude of bond alternation has a more shortwave colouration and smaller vinylene shifts; stronger absorption and somewhat larger values of the parameter V are characteristic of the less stable form. Table 1 lists the band maxima of vinylogous series of polyenes 10–12 with TG of various electron donor ability for which two forms are known.

Table 1. The maxima of the absorption bands for different forms of polyenes **10–12** (nm).^{73, 75}

PC	Φ_0 /deg.	n	$(N + 2)$ -form, $z = 0$		N -form, $z = 2 +$		$\Delta\lambda^a$
			$\lambda_{\max}$	V	$\lambda_{\max}$	V	
10	76	1	405	—	329	—	76
	76	2	428	23	351	22	77
11	40	1	413	—	459	—	–46
	40	2	430	17	497	39	–67
	40	3	444	14	526	29	–82
	40	4	465	21	554	28	–89
12	27	0	310	—	448	—	–138
	27	1	337	27	486	38	–149
	27	2	359	22	522	36	–163
	27	3	385	26	536	13	–150
	27	4	410	25	575	40	–165
	27	5	423	13	613	38	–190

^a $\Delta\lambda = \lambda_{\max}[(N + 2)\text{-form}] - \lambda_{\max}[N\text{-form}]$.

**10****11****12**

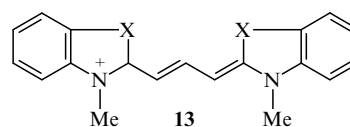
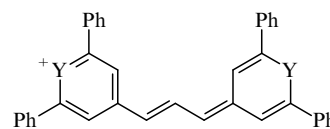
As seen from Table 1, it is stable dications of polyenes **10** with strongly electron donating benzimidazole residues that are more highly coloured and for polyenes **12** with low electron donating β -indole nuclei, it is neutral molecules that are more highly coloured. The difference between the maxima of the absorption bands of different forms increases as PC lengthens and the number of alternating bonds increases.

3. Lengthening of chromophore at the expense of terminal groups

The energy of PET is known to be significantly affected by, both the length of PC and the topology of TG.^{5, 12, 48, 49, 88, 104, 112, 113} Thus, carbocyanines **1** absorb in the range of 500–600 nm,⁸⁸ and dyes **14** with the same length of PC absorb in the range of 600–800 nm (Scheme 1).¹¹⁹

In the framework of the colour theory, it is convenient to consider this effect of TG as an effective lengthening of the polymethine chromophore.¹⁰ Various empirical increments were proposed for its quantitative estimation.^{49, 120–125} They appeared

Scheme 1

**13****14**

X	$\lambda_{\max}$ /nm
CH=CH	607
CMe ₂	545
NMe	496
O	485
S	557

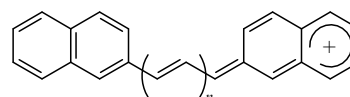
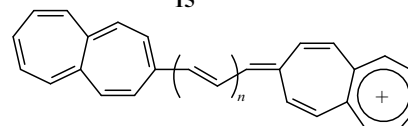
Y	$\lambda_{\max}$ /nm
NMe	638
O	676
S	755
Se	795

to remain approximately constant for the entire vinylogous series. However, they can be used only for the analysis of novel members of vinylogous series of LCS; empirical increments are hardly suitable for prediction of energies of transitions in compounds that have not been synthesised yet. The topological index of the first order L coined in the approximation of long polymethines^{42–47} appeared to be more convenient for the theoretical determination of the effect of TG on spectral characteristics of LCS. In this case, the wavelength of PET can be written as

$$\lambda_n = V(n + L). \quad (15)$$

This formula allows the understanding of the physical meaning of the parameter L : this is an effective length of TG expressed as an equivalent number of vinylene groups.

In the case of TG with the linear non-branched π -electron system, the effective length L is proportional to the actual dimensions of the molecule. For complex cyclic systems, it can be less than the real range of delocalisation of electron as it is, for example, in dyes **15** ($L = 2.7$) or exceed it significantly as in dyes **16** ($L = 12$).

**15****16**

The effective length L shows how many vinylene groups the model LCS with equalised bonds should contain for its first absorption band to fall in the same spectral range as the band of a dye with the given TG. Since the index L is calculated from formula (5), it reflects mathematically correctly such topological factors of TG as linearity or branching of the π -system; the presence, the number, position and size of the rings; the position of attachment of PC, the location and characteristics of heteroatoms and heterobonds.^{12, 42–46}

The concept of effective length of TG appeared to be useful for both the interpretation of the regularities observed in the spectra of LCS and for the search for novel compounds with the required spectral properties, in particular, dyes absorbing in the near IR range. A deep colour can be ensured mainly by two routes: by lengthening of the polymethine chromophore due to the introduction of additional vinylene groups into PC and by the introduction of TG with a large effective length.

The second route is more promising since dyes with a long open chain are not stable as the possibility of rotation about CC bonds increases, which leads to a sharp decrease in the efficiency of sensitisation and quantum yield of fluorescence. The combination of both approaches, *viz.*, the use of a long PC fixed rigidly by polymethylene bridges, and the use of pyrylium residues and its

heteroanalogues or benzo[*c,d*]indolium with a relatively large effective length, allows the absorption range of 1300–1500 nm to be achieved.^{5, 23, 24, 113, 126–133}

Systematic theoretical studies of the effect of the topology of TG on transition energies in LCS, in particular, the effect of cyclization of a part of PC,^{12, 45, 134} annelation of TG^{135–138} can be performed using the parameter *L*. In many cases, expressions for the indices Φ_0 and *L* can be written in the convenient analytical form.

4. Asymmetrical systems

The violation of the symmetry of LCS influences significantly the electronic transitions, spectral effects depending markedly on the type of compound.

Asymmetrical LCS are usually considered as derivatives of the corresponding symmetrical compounds, which are usually referred to the as parent compounds (see, for example,^{5, 9, 48–50, 139}). In the construction of asymmetrical systems, a half of the molecule is taken from one symmetrical parent compound, the other half is taken from another parent compound. If the initial systems, PMD and HP, belong to the same class, an asymmetrical system of the same class is obtained, *viz.*, polymethine or polyene, respectively; if the classes do not coincide, this gives a system of the opposite type. However, in the case of asymmetrical HP, the ambiguity arises because at least two forms of polyenes differing by a pair of π -electrons have a stable electronic shell.

In order to estimate quantitatively the degree of asymmetry, deviations *D* are traditionally used, which can be calculated in the following way:^{9, 48}

$$D = \frac{\lambda_1 + \lambda_2}{2} - \lambda_a, \quad (16)$$

where λ_1 and λ_2 are absorption maxima of the corresponding symmetrical parent systems, λ_a is the absorption maximum of the asymmetrical molecule.

Kiprianov and Pilyugin¹⁴⁰ and independently Brooker⁴⁸ have observed that for polymethine dyes $D > 0$, *i.e.* the position of the maximum for an asymmetrical dye λ_a is shifted towards short wavelengths as compared to the arithmetic mean value from the maxima of the mother dyes λ_1 and λ_2 . Thus can be rationalised by the fact that if TG are non-equivalent, the alternation of longer and shorter bonds arises in PC.

Energies of transitions and deviations in asymmetrical LCS can be determined from both absorption and fluorescence spectra; the difference consists in the structure of the initial state.

a. Absorption spectra

Specific features of absorption spectra of asymmetrical LCS are determined by the specific features of populations of bonds in a polymethine chromophore in the ground state.

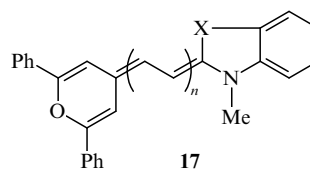
As was shown above, the bonds with a larger or smaller order alternate in PC of asymmetrical PMD; the amplitude of the alternation of π -populations of neighbouring bonds (bond orders) is proportional to the difference in basicities of TG or the difference $\Delta\Phi_{12}$. Accordingly, deviations of absorption bands also increase.^{9, 48–50} In asymmetrical chromophore, however, the alternation of populations of bonds from the centre to the ends can additionally arise if the electron donor ability φ_0 differs from the average value of 45°. That is why deviations are sensitive not only to the difference in the topological indices $\Delta\Phi_{12}$, but also to the parameter φ_0 , which relates to indices of TG in the case of asymmetrical PMD in the following way:

$$\varphi_0 = \frac{\Phi_{01} + \Phi_{02}}{2}.$$

Deviations appear to be a maximum if $\Phi_{01} > 45^\circ$ and $\Phi_{02} < 45^\circ$. In this case the alternation of bonds in the vicinity of nuclei is

synchronous with that along the chain, and its amplitude is maximum at a given $\Delta\Phi_{12}$ difference. If both TGs have either increased ($\Phi_{01} > 45^\circ$, $\Phi_{02} > 45^\circ$) or decreased ($\Phi_{01} < 45^\circ$, $\Phi_{02} < 45^\circ$) basicity, the alternation is weakened, and the deviations in these PMD are practically lacking (or insignificant), though they still grow somewhat as the $\Delta\Phi_{12}$ difference grows.^{9, 48, 141, 142}

The violation of symmetry in polyenes leads to the opposite change in bond orders as compared to that in PMD: bonds in asymmetrical HP are more equalised than in the corresponding parent compounds. For this reason, the deviations calculated from formula (16) should be negative, which was proved by experimental studies of vinylogous series of asymmetrical polyenes (17) with one constant nucleus and variable residues.^{143, 144} The spectral characteristics are listed in Table 2.



As is seen from the presented data, the deviations are really negative, *i.e.* the absorption maximum of an asymmetrical poly-

Table 2. Spectral characteristics of asymmetrical polyenes 17.¹⁴⁴

X ^a	Φ_{02} /deg	<i>n</i>	$\lambda_{\max}$ /nm	<i>V</i> /nm	<i>D</i>
CMe ₂	45	0	442	—	–18
		1	472	30	–8.5
		2	495	23	–7.5
S	56	0	454	—	–24.5
		1	483.5	29	–10
		2	506	29.5	–13
CH=CH	55	0	456.5	—	–80.5
		1	495	38.5	–36.5
		2	515.5	20.5	–32.5

^a The value Φ_{01} for all considered polyenes is 44.

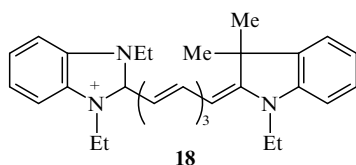
ene is shifted to the long wavelength range as compared to the arithmetic mean from the maxima of the corresponding symmetrical parent HP. The absolute value *D* increases regularly with an increase in the topological index Φ_0 of the variable residue in the series indolenine–benzothiazol–2-quinoline.

b. Emission spectra.

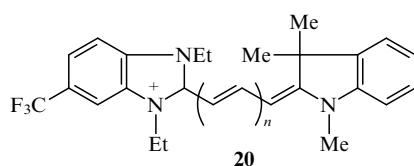
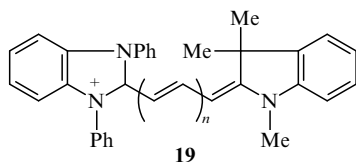
Specific features of the structure of the excited state should influence the energies of transitions determined from fluorescence spectra. As was mentioned above, in the case of asymmetrical LCS, bond orders equalise substantially on excitation. For this reason, emission spectra are remarkably less sensitive to the violation of symmetry, and the additive formula should be true for them

$$\lambda_n^{\text{fl}} = V^{\text{fl}} \left(n + \frac{L_1 + L_2}{2} \right). \quad (17)$$

An analysis of the spectra has shown that deviations of the maxima of fluorescence are 1–2 orders of magnitude less than those of absorption maxima.^{23, 24, 106, 107} Thus, for dye 18 with a rather long PC, the deviation calculated from the absorption spectra is 176 nm whereas that of the fluorescence maximum is only 3 nm.¹⁰⁶



The studies of vinylogous series of asymmetric of dyes **19** and **20**



have shown that the contribution of PC also appears to be additive.^{24, 106, 107, 145–147} As is seen from the data of Table 3, the V^{fl} parameter is virtually equal to 100 nm and changes little with the lengthening of PC while V is significantly smaller and decreases on going to higher vinylogues.

The alternation of bonds in polyenes and asymmetrical polymethines leads to the formation of photoisomers in the excited

Table 3. Spectral data for asymmetrical PMD **19** and **20** (nm).

Dye	<i>n</i>	EtOH				CH ₂ Cl ₂			
		λ_{max}	<i>V</i>	$\lambda_{\text{max}}^{\text{fl}}$	<i>V</i> ^{fl}	λ_{max}	<i>V</i>	$\lambda_{\text{max}}^{\text{fl}}$	<i>V</i> ^{fl}
The data of Ref. 107									
19	1	506	—	553	—	512	—	554	—
	2	580	74	657	104	600	88	659	105
	3	615	35	763	106	662	62	762	103
The data of Ref. 108									
20	1	450	—	517	—	450	—	517	—
	2	497	47	620	103	528	68	622	105
	3	515	18	721	101	560	32	718	96

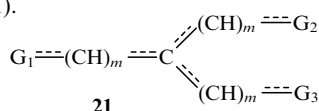
Note. The following notations are accepted: λ_{max} and $\lambda_{\text{max}}^{\text{fl}}$ are wavelengths of the absorption and fluorescence maxima, respectively; V and V^{fl} are vinylene shifts of the absorption and fluorescence bands, respectively.

state, which can appear in fluorescence spectra, especially when measured by flash spectrometry.^{148–151} Calculations show that the height of the conformational barrier depends on the nature of TG.^{148, 149, 152–154}

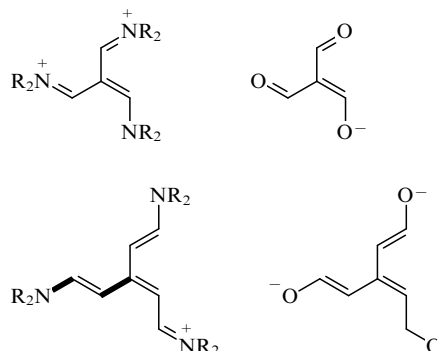
Substantial difference in the energies of transitions observed in the absorption and emission spectra is used in practice for the creation of dyes with large Stokes shifts. These dyes are applied in quantum electronics (see, for example, review²⁴).

5. Branching of a chromophore

Symmetrical branching of a chromophore observed in the so-called tri-nuclear dyes (TPMD) is of special interest. The effect of this change in molecular topology manifests itself most clearly (**21**).



Simultaneous lengthening of each branch of PC yields homologous series of TPMD. A stable closed electronic shell is characteristic of TPMD in the form of monocations (monoanions) or dications (dianions), as for example,



If all three TGs have identical structures, the ion of TPMD in the ground state has the C_3 symmetry, which is confirmed by the ¹³C NMR spectra.^{155, 156} In the crystalline state, the C_3 symmetry is maintained only for single-charged dyes having one counterion; in the case of TPMD with two counterions, this symmetry is violated.¹⁵⁶ The C_3 symmetry of the chromophore leads to the degeneracy of the antisymmetrical MO. For TPMD with an even number of methine groups m , the LUMO is degenerate in each branch, for those with an odd m , the HOMO is degenerate.

Note that branching of a chromophore is also possible if a central cycle, three-^{158, 159} or four-membered¹⁶⁰ one, is introduced.

a. Trimethine shifts

The degeneracy of one of the boundary orbitals leads to the degeneracy of PET; therefore, two transitions are responsible for the observed longwave band.^{161, 162} The violation of the equivalence of bonds in branched PC causes broadening of absorption bands (to 1300–1500 cm^{−1})¹⁶² as compared to PMD with two TGs (~ 900 cm^{−1}).¹⁶³

The contribution of PC into the wavelength of PET in the case of TPMD is evaluated as the so-called trimethine shift T

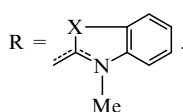
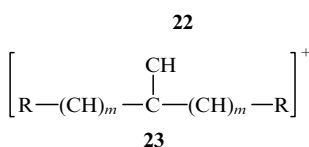
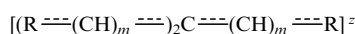
$$T = \lambda_m - \lambda_{m-1}. \quad (18)$$

It has been shown¹⁶⁴ that the parameter T depends on the parity of the number of the methine groups the topological index m and Φ_0

$$T = V + (-1)^m \Delta \left(\frac{\pi}{2} - 2\Phi_0 \right), \quad (19)$$

where $\Delta = V/3\pi \approx 10$ nm.

Due to the $(-1)^m$ multiple the trimethine shift alternately exceeds or is less than as the vinylene shift V , which is in accordance with the experimental data for TPMD **22** with indolenine residues (Table 4).



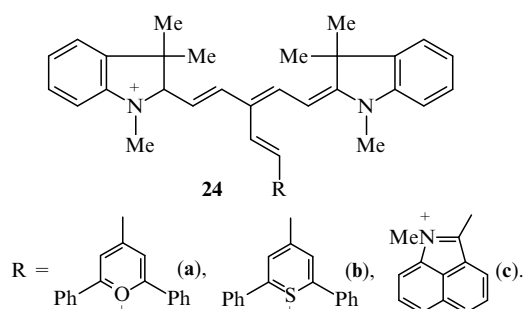
The data presented in Table 4 also confirm that the trimethine shift depends on the Φ_0 index.

Table 4. Spectral characteristics of trinuclear (TPMD) **22** and binuclear (BPMD) **23** dyes (nm).¹⁵⁷

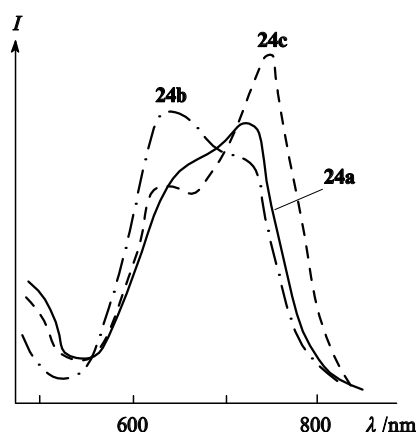
X	<i>m</i>	TPMD (22)			DPMD (23)	
		<i>z</i>	$\lambda_{\max}$	<i>T</i>	$\lambda_{\max}$	<i>V</i>
CMe ₂	1	+1	522	—	544	—
	2	+2	635	83	636	90
	3	+1	755	120	745	109
S	1	+1	534	—	556	—
	2	+2	635	101	650	94
CH=CH	1	+1	678	—	708	—
	2	+2	788	110	813	92

b. Asymmetrical trinuclear polymethine dyes

The violation of the C_3 symmetry lowers the degeneracy of MO and, hence, the degeneracy of electronic transitions; the splitting of the levels is proportional to the difference between the effective lengths of TG. When the topological indices differ sufficiently, two transitions in asymmetrical TPMD can manifest themselves in the spectra as separate maxima, which was observed for asymmetrical [2.2.2]heptamethinecyanines **24** containing two identical TGs and one differing in structure.^{161, 162}



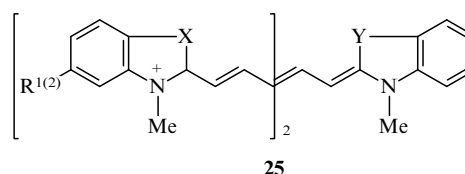
If effective lengths of the nuclei differ insignificantly (for 2-quinoline, benzothiazole, benzimidazole, $L = 3.0-3.5$), the absorption band has one maximum. The introduction of residues with a relatively high L value such as pyrylium (6.06), thiopyrylium (7.26), benzo[*c,d*]indole (6.50), causes splitting of the absorption band (Fig. 5).

**Figure 5.** Absorption spectra of asymmetrical trinuclear dyes **24a-c**.**c. Excited states**

Population of the degenerate excited state of symmetrical TPMD should be accompanied, according to the Jahn–Teller rule, by a significant change in the molecular geometry. If lifetime of the excited state is sufficiently long, one of the branches of TPMD

deviates from the plane, and the symmetry of the chromophore lowers. It was pointed in a number of publications^{156, 157, 165–167} that in the excited state one of the branches is located perpendicular to the plane of the rest of the molecule. Similar situation seems to occur in asymmetrical TPMD with symmetrical branching of PC at a small splitting of the energies of the states.

If TPMD contains one nucleus differing from the others, two conformers are possible: one corresponds to symmetrical binuclear dye with a substituent in the meso position, the other corresponds to the meso-substituted asymmetrical dye. A substantial change in geometry upon excitation leads also to significant Stokes shifts $\Delta\nu_C$. Table 5 lists the luminescence spectral data for asymmetrical TPMD **25**. The Stokes shifts are in fact greater than those for binuclear dyes for which $\Delta\nu_C$ is 400–500 cm^{-1} . In the case of TPMD **25c** and **25h** bearing TG with significantly different basicities (indolenine, benzimidazole), two conformers with different fluorescence maxima were observed.^{162, 168}

**Table 5.** Spectral characteristics of TPMD **25**.^{162, 168}

Type of dye 25	X	Y	R ¹	R ²	$\lambda_{\max}$ /nm	$\lambda_{\max}^{\text{fl}}$ /nm	$\Delta\nu_C$ / cm^{-1}
a	S	S	H	H	632	639	1517
b	CH=CH	S	H	H	666	735	1390
c	S	CH=CH	H	H	636	709	1610
d	CH=CH	CH=CH	H	H	690	759	1318
e	CMe ₂	CMe ₂	H	H	628	698	1616
f	NPh	NPh	CN	CN	605	652	1176
g	CMe ₂	NPh	H	CN	630	654	1464
h	NPh	CMe ₂	CN	H	556	626	2901

IV. Changes in the structure of the polymethine chromophore

In addition to the basic topological factors that were comprehensively considered above, the energy of PET is appreciably influenced by such changes in the structure of polymethine chromophore as substitution of the methine groups by heteroatoms, introduction of substituents and the acetylene-cumulene bond, steric hindrances, cyclization of a part of PC, etc. These effects can be interpreted relatively reasonably within the framework of perturbation theory.^{169–174} The final expressions resemble the well-known Hammett relationship

$$\Delta\lambda_{\max} = \rho\sigma, \quad (20)$$

where $\Delta\lambda_{\max}$ is the spectral effect of perturbation, ρ is the change in the electronic structure of the chromophore upon excitation, and σ is the magnitude of perturbation.

Let us consider the most important types of perturbations of the structure of chromophore.

1. Replacement of methine groups by heteroatoms.

Within the framework of perturbation theory, this change in the structure can be simulated by varying the electronegativity of the μ th atom or more precisely, the h_μ Coulomb integral. A change in

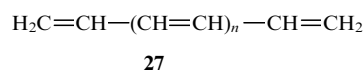
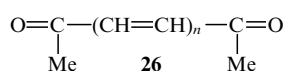
the wavelength of PET appear to be proportional to a change in the electron density (Δ_μ) upon excitation.^{170–172}

$$\Delta\lambda = a\Delta_\mu h_\mu, \quad (21)$$

where

$$a = \frac{V(n+L)^2}{\pi}.$$

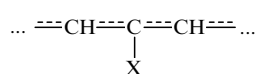
It was shown above that PMD are characterised by a remarkable changes in atomic populations during electronic transitions, whereas in HP chromophore Δ_μ values are substantially smaller. As a result, the heterosubstitution in polyenes affects the spectra much less. Thus the spectral effect of the replacement of the methine group by the nitrogen atom in PMD can exceed 100–120 nm, especially for the middle of the chain; on approaching the nuclei, the maximum is less shifted.^{5, 9, 10, 170–172, 175} The changes in the spectra of polyenes are much less. Moreover, it should be taken into account that for HP the influence of the change in the degree of conjugation of the heterobond relative to the CC bond can overlap the effect of changes in electronegativity of the atom. It is the case, for example, for α,ω -diketones **26** in comparison to polyenes **27**.



n	$\lambda_{\text{max}}/\text{nm}$	$\Delta\lambda/\text{nm}$	
	26 ¹¹⁸	27 ¹⁰⁴	
1	228	256	−28
2	278	289	−11
3	328	317	+11
4	351	343	+8
5	380	366	+14
6	406	384	+22

2. Conjugated substituents

Heteroatom X with a lone electron pair can be an example of the simplest conjugated substituent.



X = F, Cl, Br, OR, SR, NR₂ ...

If the distance between the levels of a substituent and the boundary levels of the polymethine chromophore is significantly less than the energy gap, the formula for the displacement of the $\Delta\lambda$ maximum resembles formula (21). In the general case, with $\lambda = V(n+L)$, the formula can be written for the middle of the chain

$$\Delta\lambda = (-1)^{n+\mu+1} \left(\frac{\lambda_{\text{max}}^0}{\pi} \right) \delta_X;$$

$$\delta_X = \frac{C_{vj}^2}{\varepsilon_j} \beta_{CX}, \quad (22)$$

where atoms are numbered from the midpoint of PC, so that $\mu = 0$ for the meso position. The parameter δ_X characterises numerically the effect of the substituent: β_{CX} is the resonance integral between substituent X and the chromophore, C_{vj} is a coefficient of the j th MO of the substituent at the v th atom bound to the μ th atom of the chromophore, and ε_j is the energy of the level of substituent.

Formula (22) reflexes qualitatively the known Förster–Dewar–Nott rule^{172–174} concerning the direction of the shift of the longwave absorption band depending on the nature and the place of perturbation: the introduction of donor substituents ($\delta_X > 0$) or replacement of the methine groups by more electronegative atoms ($h_\mu > 0$) in the meso- and vinylogous positions (*i.e.* in the positions with the same parity, μ is even) in dyes A lead to bathochromic effects; on the contrary, the introduction of acceptor substituents ($\delta_X < 0$) or heterosubstitution by less electronegative atoms ($h_\mu < 0$) is accompanied under the same conditions by a shift of the maximum of the absorption band towards the shortwave region. For neighbouring positions and upon changing the class (*i.e.* the change in the number of vinylyne groups n in PC), the sign of the effect changes to the opposite, which is confirmed by a large body of experimental observations.^{88, 170, 176, 177}

Note that for a more rigorous quantitative estimate, the inductive effect of substituents should be also taken into account. Thus the following correlational equation connecting the absorption frequency for thiocarbocyanines with the constants of resonance δ_{res} and inductive δ_{ind} interactions was found:^{176, 178}

$$\Delta\nu = 67 - 1170(\delta_{\text{ind}} + 5.28\delta_{\text{res}}). \quad (23)$$

3. Rules of sensitivity

Spectral effects are rather sensitive to electron donor ability of LCS for the effect of conjugated substituents depends clearly on the distance between the interacting levels. A study of the influence of polar groups in thiazole and benzthiazole dyes¹⁷⁹ has shown that the spectral effect of electron donor groups decreases with an increase in the basicity of the dyes, and vice versa, the effect of electron-withdrawing substituents decreases under identical conditions.

Indeed, in PMD with high electron donor ability for which Φ_0 , $\varphi_0 > 45^\circ$, the boundary levels are up-shifted and located nearer to the vacant level of the electron-accepting substituent (for instance, cyano or nitro group). And on the contrary, the boundary levels appear to be distant from the occupied level of the donor substituent. Since the interaction between the levels is inversely proportional to the distance between them, these dyes, other conditions being identical, are more sensitive to acceptor substituents; on the contrary, donor substituents cause smaller shifts of the absorption band.

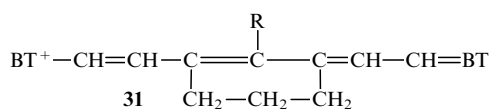
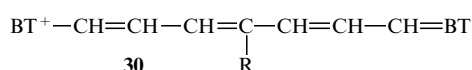
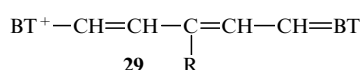
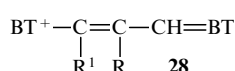
In dyes with a decreased electron donor ability (Φ_0 , $\varphi_0 < 45^\circ$), the boundary levels are located nearer to the level of the donor substituent. For this reason, these dyes are more sensitive to similar substituents. Acceptor substituents should cause lesser effect, for their levels are more remote from the boundary levels responsible for the electronic transition. PMD, derivatives of benzo[*c,d*]indole with a decreased electron donor ability can provide the experimental evidence;¹⁸⁰ the introduction of donor groups leads to a larger shift of the maximum of the absorption band than the introduction of the electron-withdrawing nitro group.

Another rule concerns the magnitude of hypsochromic and bathochromic effects. An analysis of energies of transitions and mutual location of a chromophore and a substituent shows that the bathochromic shifts of the band of PET result from the interaction between the level of the substituent (both donor and acceptor) and the boundary level that is located closer to it, and hypsochromic shifts result from the interaction with the substituent having the more distant level. Bearing in mind that the levels usually repel and the shift of levels is inversely related to the distance between them, the following rule can be formulated: the introduction of conjugated substituents should cause larger, other conditions being identical, bathochromic shifts of absorption bands in the spectra, the difference between the values of the bathochromic and hypsochromic shifts being the larger, the greater is the energy gap.

Table 6. Spectral data for chromophore-substituted PMD **28–31**.

Dye	R	R ¹	$\lambda_{\max}$ /nm	$\Delta\lambda$ /nm
The data of Ref. 176				
28	H	H	556	—
	CN	H	610	+ 54
	H	CN	529	–33
29	H	—	636	—
	CN	—	613	–23
The data of Ref. 181				
30	H	—	758	—
	CN	—	810	+ 52
31	H	—	766	—
	CN	—	884	+ 118

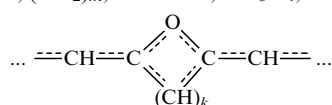
This can be illustrated by the spectral data for cyano-substituted thiacyanines (BT is the benzothiazole residue) presented in Table 6.



In the case of heterosubstitution, the absolute values of the hypsochromic shifts appear to be bigger than those of the bathochromic shifts due to the alternation of bonds arising in the chromophore.^{171, 175}

4. Cyclisation of a part of the chain

Let us consider a fragment of the chromophore in which the bridge Q can be an ordinary bond, an atom (O, S), or a group of atoms (NR, (CH₂)_m, CH = CH, *o*-C₆H₄, etc.).



Spectral effects of symmetrical cyclization can be predicted.¹⁸² The influence of cyclization with involvement of a single bond can be simulated within the framework of perturbation theory by increasing the resonance integral from zero to some finite value. Spectral effects may be rather significant (of the order of 100–200 nm).^{10, 182}

The formation of cycles *via* bridges resembles the introduction of conjugated substituents with the only difference that two bonds are used instead of one. However, it is an increase in the number of bonds formed between the reacting systems (the chromophore and the bridge) that determines the principal difference on cyclization.

The change in the energy of MO upon cyclization is described by the general formula:

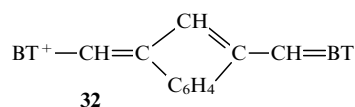
$$\varepsilon_i = \sum_j \frac{1}{\varepsilon_i - \varepsilon_j} \left(\sum_{\mu} \sum_{\nu} C_{i\mu} C_{j\nu} \beta_{\mu\nu} \right)^2, \quad (24)$$

where ε_i and $C_{i\mu}$ are energy and coefficients of MO of the chromophore, respectively, ε_j is energy, and $C_{j\nu}$ are coefficients of the MO of the bridge Q; $\beta_{\mu\nu}$ are resonance integrals of the bonds formed upon cyclization.

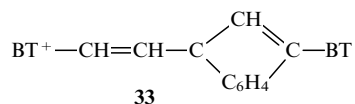
Analysis of the formula (24) shows that the effect of cyclization differs from the sum of effects of two conjugated substituents by a factor that includes the composition of the coefficients of four atoms μ , μ' and ν , ν' involved in the formation of two bonds between the chromophore and the bridge: $2C_{i\mu}C_{i\mu'}C_{j\nu}C_{j\nu'}$. Hence, not only the signs of populations of orbitals on atoms determined by squares of coefficients are clearly taken into account, as in the case of substituents, but also the signs of the coefficients of MO. With regard to whether the signs of the coefficients coincide or not, the effect of cyclization can either exceed the overall effect of substituents or be practically absent as is proved experimentally using the cyclization *via o*-phenylene,^{183–186} vinylene,^{187, 188} and polymethylene^{64, 126, 181, 187, 188} bridges as examples.

Polyphenylenes and polyphenylenevinylene can be considered as polyenes with the vinylene bridges.¹⁸⁹ This change in the topology of PC leads to an increase in the energy gap. Analogous cyclization *via* the sulfur atoms is followed by a shift of zones of the levels.^{190, 191} This case, local levels of substituents appear between the zones, and the electronic transition is accompanied by the electron transfer through the conjugation chain. This phenomenon finds wide application in molecular electronics.^{191–193}

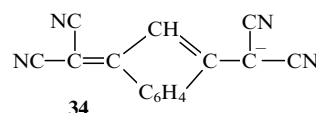
The above-formulated rule about a bigger absolute value of the bathochromic shifts of the absorption band is true for spectral effects of cyclization. To illustrate this, below are given formulae of thiacyanines¹⁸⁴ **32**, **33** and malocyanines¹⁸³ **34**, **35** with the *o*-phenylene bridge in PC that obey this rule.



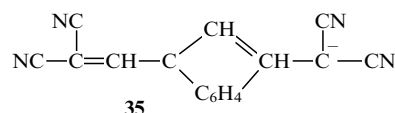
$$\lambda_{\max} = 755, \Delta\lambda = +100 \text{ nm}$$



$$\lambda_{\max} = 615, \Delta\lambda = -40 \text{ nm}$$



$$\lambda_{\max} = 630, \Delta\lambda = +290 \text{ nm}$$



$$\lambda_{\max} = 534, \Delta\lambda = -30 \text{ nm}$$

5. Change in the resonance interaction

A change in the conjugation takes place in the case of steric hindrances, with the introduction of acetylene/cumulene bonds and heterobonds, for example, $-\text{N}=\text{N}-$, $-\text{P}=\text{P}-$, etc. These perturbations can be conveniently simulated by varying the resonance integral $\delta\beta_{\mu\nu}$. Then the change in the energies of MO ($\delta\varepsilon_i$) and the wavelength of PET ($\delta\lambda$) will be written in the form^{10, 12, 170, 171}

$$\delta\varepsilon_i = 2 \sum_{\mu\nu} C_{i\mu} C_{i\nu} \delta\beta_{\mu\nu}, \quad (25)$$

$$\Delta\lambda = -b \sum_{\mu\nu} \Delta_{\mu\nu} \delta\beta_{\mu\nu}, \quad (26)$$

where $b = 2(V/\pi)(n + L)^2$, and $\Delta_{\mu\nu} = \rho_{\mu\nu}^* - \rho_{\mu\nu}^0$ is the change in the order of the bond being varied in the excitation.

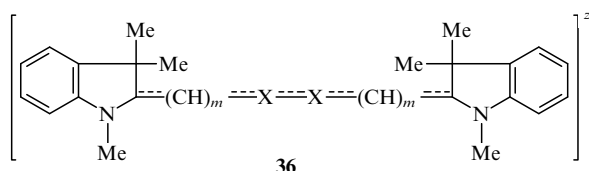
Since in polymethines the nodes of the boundary orbitals are located in the vicinity of atoms and in polyenes they are located near the middle of the bonds, the influence of the change in the resonance interaction between neighbouring atoms ($\nu = \mu \pm 1$) should be substantially less for PMD than for HP.

Spectral effects arising in PMD with steric hindrances and upon the introduction of an acetylene bond have been comprehensively studied.^{5, 9, 171, 194–198} The shift of the absorption maximum was found to depend on the basicity of TG (especially strongly in the perturbations at the ends of PC). However, for polymethines with a medium electron donor ability, the sign of the effect in the middle of the chain depends only on the nature of perturbation.^{171, 194}

Changes in the spectra of HP differ in principle. The analysis of formulae (25) and (26) and the signs of the boundary MO allow one to formulate the following rule: an increase in the resonance interaction along the formally double bond of PC in HP is accompanied by a hypsochromic shift, and that along the formally ordinary bond causes a bathochromic shift of the absorption band; a decrease in the resonance interaction along the formally double bond leads to bathochromic shifts, that along the ordinary bond results in a hypsochromic shift of the maximum.

Spectral data for acetylenes and cumulenes serve as the best experimental evidence. The introduction of additional π -bonds perpendicular to the major π -system in these compounds leads to a change in the CC bond lengths; in this case electronegativity of the atoms changes: for acetylenes the hypsochromic shifts, and for cumulenes the bathochromic shifts are observed.⁸⁸

If in PC of symmetrical polyenes only the central bond is substituted, the sign of the effect depends on the class of the compound. It can be illustrated by the data of Table 7 for indopolyenes **36** the longwave band of which is reliably assigned to the polymethine band.



As is seen from the data presented, the sign of the effect changes every time in accordance with the above-formulated rule, when the class of HP is somehow changed: either by change in the chain length or by change in the number of the HOMO.

Table 7. Spectral data for HP **36** (nm)^{115–117}

<i>m</i>	X	<i>(N + 2)</i> -form, <i>z</i> = 0			<i>N</i> -form, <i>z</i> = 2 +		
		class	$\lambda_{\max}$	$\Delta\lambda$	class	$\lambda_{\max}$	$\Delta\lambda$
1	CH	A	410	—	C	450	—
1	N	A	464	+ 54	C	382	– 68
2	CH	B	435	—	A	454	—
2	N	B	387	– 48	A	492	+ 38

V. Systems with several polymethine chromophores

In some cases, LCS can contain several π -systems. In addition in order to give more spectacular interpretation it is more convenient sometimes to split the common chromophore into constituents

that are responsible for individual bands. However, the spectra of molecules with several chromophores or aggregates of molecules with one chromophore differ from those of the initial systems due to the so-called interaction of chromophores.^{199, 200} The theoretical interpretation of this phenomenon is given²⁰¹ in terms of the dipole-dipole approximation. It was shown that the interaction of chromophores leads to an extension of the absorption maxima against the position of the corresponding maxima in parent chromophores. The nature of this extension can be explained using a model proposed for the analysis of the excited states of molecular crystals.²⁰²

If the system contains two chromophores having the transition energies E_a and E_b ($E_a < E_b$) and the energy of the interaction H_{ab} is small, the energies of two new transitions E_- and E_+ are determined as follows:

$$\begin{aligned} E_- &\simeq E_a - \frac{H_{ab}}{E_a - E_b}, \\ E_+ &\simeq E_b + \frac{H_{ab}}{E_a - E_b}. \end{aligned} \quad (27)$$

It is seen from these formulae that the interaction should result in the movement apart of the absorption maxima, the effect being the larger the closer the maxima are located. If the energies of the parent chromophores coincide, the formulae change somewhat

$$E_{\pm} = \frac{1}{2} \left(E_0 \pm \sqrt{E_0^2 + 4H_{ab}^2} \right). \quad (28)$$

It is impossible to say which of the bands belongs to the excitation of one chromophore and which belongs to the other. Both bands are associated with the excitation of both chromophores, but during one transition the chromophores are excited in phase, and during the other they are excited in antiphase.

In the dipole approximation, the energy of the interaction H_{ab} is calculated using the moments of transitions of the parent chromophores M_a and M_b

$$H_{ab} = \frac{e^2}{R^3} [(M_a M_b) \mathbf{R}_{ab}^2 - 2(M_a \mathbf{R}_{ab})(M_b \mathbf{R}_{ab})], \quad (29)$$

where R is the length of the $\mathbf{R}_{ab}$ vector directed from the chromophore a to the chromophore b .

If two chromophores are arranged linearly, the longwave transition appears to be more intense, if they are located in a parallel way, the shortwave transition is more intense. If the dipoles are oriented arbitrarily with a ϑ angle between them, the ratio of intensities of the longwave I_- and shortwave I_+ transitions is

$$\frac{I_-}{I_+} = \operatorname{tg}^2 \frac{\vartheta}{2}. \quad (30)$$

This approximation gives good results if the distance between chromophores exceeds their own dimensions.^{200, 201, 203}

1. Bisdyes

Widely studied bisdyes are the simplest and most convenient systems in which two PET manifest themselves in the visible and near-IR ranges of the spectrum.



37

Here M is the bonding bridge that can be both conjugated and non-conjugated. In the spectra of bisdyes of symmetric structure ($G_1 = G_4$, $G_2 = G_3$, $k = l$), the absorption band corresponding to the parent PMD splits into two bands. The distance between the split bands and the ratio of their intensities depend on the degree

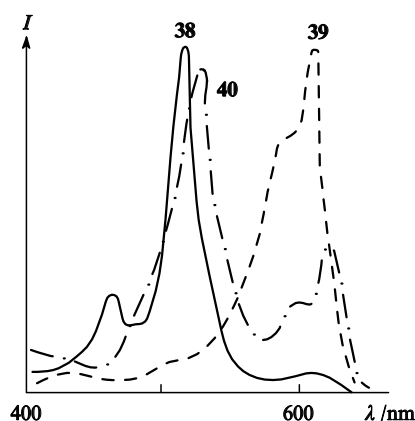
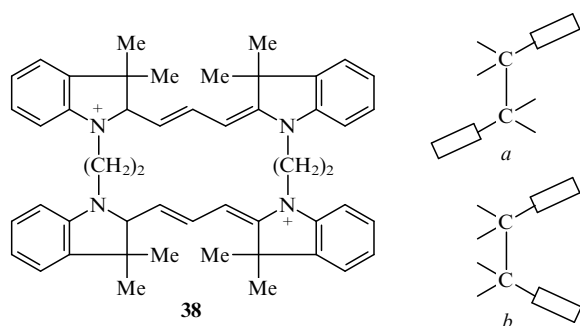


Figure 6. Absorption spectra of bisdyes 38–40.

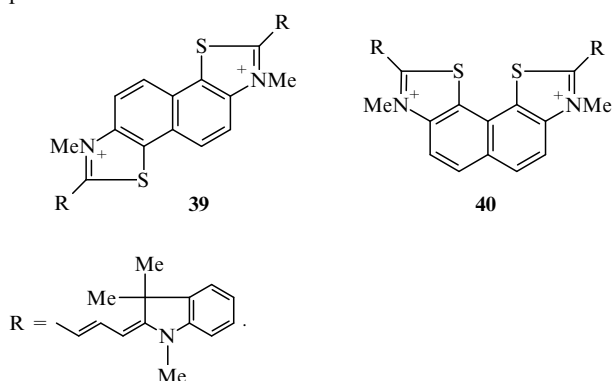
of conjugation, the distance and the angle between chromophores.^{200, 203–206}

An experimental study of cyanine dyes bound by a non-conjugated polymethylene bridge, $-(CH_2)_m-$, has shown that the distance between the first and the second maxima decreases with an increase in the number of the methylene groups.²⁰⁷ If the non-conjugated chromophores are arranged in the strictly parallel manner as in bisdyes 38, the longwave transition is symmetry forbidden ($I_- = 0$) and all the intensity is concentrated in the shortwave band (Fig. 6).²⁰⁸



Note that the spectrum of the bisdye 38 was assigned to the erroneously observed conformation *a* of the dye in which any overlap of the π -orbitals and, hence, their interaction are lacking.²⁰⁸ In fact the spectrum is in accordance with the conformation *b* with a dihedral angle between the π -systems of the chromophores of $\sim 40^\circ$ and a minimum distance of ~ 2.5 Å between the π -centres of both chromophores, which is sufficient for the effective interaction of the π -systems.

The interaction of the chromophores is more substantial in bis-dyes with conjugated bridges,^{209–212} for example, in compounds 39 and 40.



If in PMD 39 the chromophores are arranged linearly, practically all the intensity is concentrated in the longwave band (see Fig. 6). In the case of the dye 40 with a fixed acute angle between the chromophores, two bands are observed, however, according to formula (30), the band in the shortwave region is more intense.^{211, 212}

2. Aggregation of polymethine dyes

There are many publications concerning the structure and application of molecular aggregates of PMD.^{213–217}

The phenomenon of aggregation in dyes has been discovered by Scheibe²¹⁸ and Jelly.²¹⁹ PMD were found to form molecular aggregates both in solution and on the surface of certain crystals. It was shown that in aggregates the molecules of a dye are bound owing to the non-valent resonance interaction. Depending on the conditions and the molecular structure, dyes can form two main types of aggregates (*J* and *H*) that differ distinctly in the spectral properties. The maxima of the absorption bands of *J*-aggregates (*J*-bands) show a bathochromic shift whereas the maxima of the absorption bands of *H*-aggregates (*H*-bands) show a hypsochromic shift relative to the band maxima of isolated molecules (*M*-bands).

It was found that *J*- and *H*-aggregates differ in the value of the angle between the long axis of the chromophore and the axis of the molecular aggregate.^{218, 220, 221} In accordance with the theory of interaction of chromophores, different orientation of molecules in the corresponding aggregates leads to the appearance of very intense and very narrow longwave bands in the spectra of *J*-aggregates, unlike the spectra of *H*-aggregates.

It should be noted that the nature of a solvent, the type of the surface of the ionic crystal and some other factors can affect appreciably the aggregation of dyes.^{17, 213–215}

VI. Terminal groups as local chromophores

If LCS contain complex conjugated TG with their own strong absorption in addition to the band corresponding to the polymethine chromophore, the bands resulted from the transitions from the orbitals localised predominantly in the terminal nuclei appear in the spectra; therefore, TG can be conventionally considered as local chromophores.

Within the orbital approximation, the simplest type of local transitions is described by the local level and one of polymethine levels delocalised over the whole molecule of LCS (Fig. 7 *a–d*). As a result, LET and PET should interact strongly. The assignment of the band to polymethine chromophores depends on which transition, PET or LET, has the lowest energy.

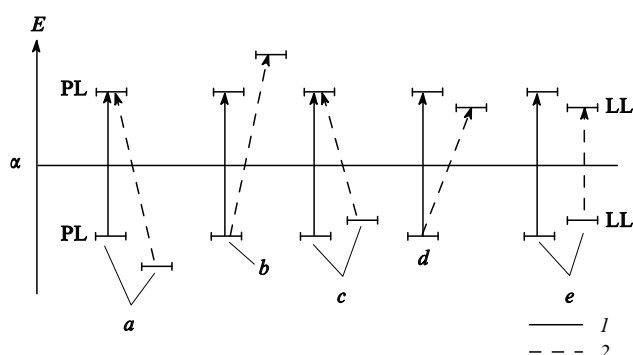
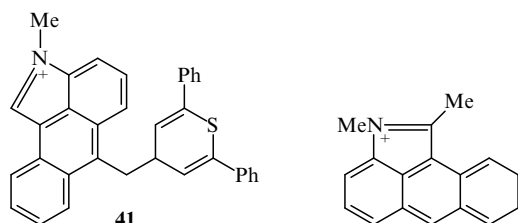


Figure 7. The position of polymethine (PL) and local (LL) levels in LCS with local chromophores (*a–d*) and in bis-dyes (*e*); (1) PET, (2) LET.

1. Local transitions in PMD

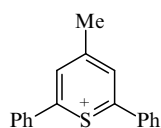
In the case of typical PMD, delocalised polymethine levels are usually arranged nearer to the Fermi level than the local level (see Fig. 7 *a, b*). The first transition has the polymethine character, the

second is mainly localised in TG. Asymmetrical cyanines, derivatives of thiazolopyridinium,^{222–224} thiazolopyrimidinium,^{225–227} 2,6-diphenylpyrylium and its heteroanalogues^{228, 229} are compounds with this arrangement of the levels. If both residues have relatively intense absorption of their own as, for instance, in dye **41**, both nuclei can be regarded as local chromophores.²³⁰



$\lambda_{\max} = 784; 500; 384 \text{ nm}$

$\lambda_{\max} = 543 \text{ nm}$



$\lambda_{\max} = 410 \text{ nm}$

Calculations have shown that the first transition is delocalised over the whole molecule, the atoms of the pyrroloanthracene moiety participate predominantly in the second, and atoms of the thiapyrylium nucleus take part in the third.

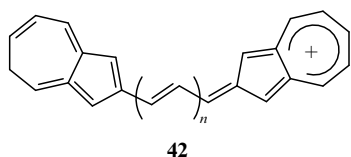
Lengthening of PC little affects the localised levels, however, the polymethine level regularly approaches the Fermi level. For this reason, the band responsible for LET undergoes a bathochromic shift as well as the band corresponding to PET, but the magnitude of this shift is less than that of the vinylene shift of the polymethine band.^{81, 222–227, 231}

Symmetrical PMD contain two identical local chromophores. If they do not interact as, for example, in α, ω -di(1-azulenyl)polymethines, the second band observed experimentally is responsible for two practically degenerate LETs.⁸¹ If local chromophores do interact, the bands split, as was observed for symmetrical cyanine dyes, derivatives of thiazolopyridinium.²³¹

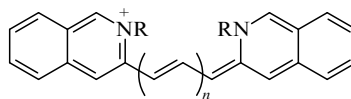
2. Inversion of local and polymethine electronic transitions

If local levels appear nearer to the Fermi level than in polymethines (Fig. 7 c,d), the local transition has the lowest energy, *i.e.* the inversion of the transitions takes place. The following conditions are necessary for the inversion of PET and LET: TG should have a level located near the Fermi level (it is usually the case when the initial heterocycle is deeply coloured); a relatively big distance between the polymethine levels; a shift of polymethine levels towards the local level (it occurs if PMD contains either strongly basic or weakly basic nuclei, *i.e.* when the Φ_0 index takes the values close to the limiting, 0 or 90°).

These conditions are realised, for example, in α, ω -di(2-azulenyl)polymethines **42** ($\Phi_0 = 0^\circ$) or **43** with residues of isoquinoline ($\Phi_0 = 80^\circ$).

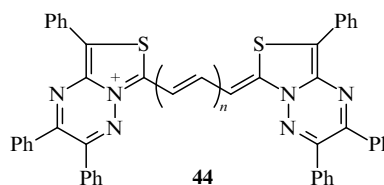


42



43

It has been shown that two first transitions are mainly localised on the atoms of the terminal group (though the atoms in the odd positions also participate in them), which can be conventionally considered as conjugated substituent of the local chromophore. These transitions are characterised by smaller vinylene shifts as compared to the third transition localised in the polymethine chromophore.⁸¹ The polymethine levels come closer together regularly with an increase in the number of vinylene groups, while the position of the local level changes little. Consequently, lengthening of the chain can be accompanied by a change in the nature of transitions.⁸¹



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The inversion of PET and LET was observed experimentally in triazotriazine dyes **44**.²²⁴ As is seen from Fig. 8, the contour of the shortwave band is close to those of the longwave bands corresponding to PET in typical PMD. Obviously, the long wavelength band in the case of dyes **44** can be assigned to the local transition in the residues of triazotriazinium.

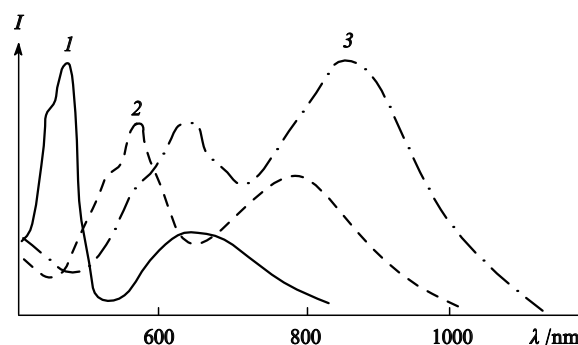


Figure 8. The absorption spectra of PMD **44**.
n: (1) 0, (2) 1, (3) 2.

3. Local transitions in heteropolymethines

A change in the type of LCS, the passage from PMD to HP, influences little the position of local levels, but affects significantly the position of polymethine levels. First, they are shifted by approximately half of the gap due to an additional π -level, up-shifted in the case of the reduced form and down-shifted in the case of the oxidised form, in accordance with formula (7). Second, the distance between the highest occupied and the lowest unoccupied polymethine levels and, therefore, the energy of PET increases additionally due to the strong alternation of bonds in PC. As a result, the inversion of electronic transitions is more probable in HP than in PMD with the same TG, especially for a small number of vinylene groups in the chain. As the length of the polymethine chromophore is increased, its levels approach the Fermi level but significantly more slowly than the polymethine levels do in PMD. Since for polyenes $\varphi_0 = \Phi_0 \pm 45^\circ$, the maximum shift of the polymethine levels is achieved when TG has a medium electron donor ability ($\Phi_0 = 45^\circ$), in contrast to PMD. α, ω -Di(1-azulenyl)polymethines and their isomers having PC in another position can serve as examples. In the spectra of these compounds in the visible and near-IR regions, two typical absorption bands were observed: a broad longwave and a more narrow, shortwave band.^{232, 233} Calculations show that the two first transitions result from excitations in local azylene chromophores, and the third is

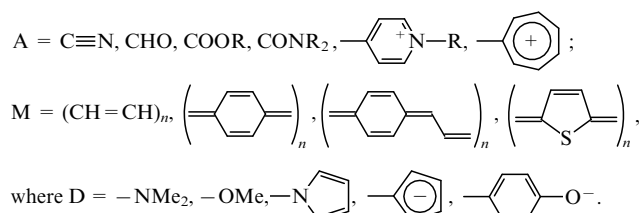
delocalised along the whole molecule of the polyene.⁸¹ Lengthening of the chain by one vinylene group practically does not change the energies of the first and the second transitions, further introduction of vinylene groups can result even in the negative vinylene shift (-8 nm). It is probably associated with the weakening of the interaction between local chromophores. The vinylene shift of the third (polymethine) transition is $30-35$ nm, which falls within the interval of values typical of PET in polyenes.

4. Local transitions in asymmetric donor-acceptor polyenes

Of especial interest is the case when both boundary levels appear to be local (Fig. 7e) and are localised in different TG as, for example, in donor-acceptor polyenes of the general formula



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In these systems, the photoexcitation is accompanied by a significant intramolecular charge transfer, the so-called photoinduced charge transfer.²³⁴⁻²³⁷ In the first approximation, the energy of the electronic transition between the localised HOMO and LUMO is determined by the difference between the ionisation potential of the donor group P_D and the electron affinity of acceptor E_A .^{39, 238-240}

$$E = P_D - E_A + C, \quad (31)$$

where C is correction for the Coulomb and resonance interactions of electrons.

Localisation of both boundary MO results, as a rule, in a lower intensity of charge transfer transitions. At the same time, the dipole moment of the molecule in the excited state increases significantly, and therefore, asymmetrical donor-acceptor systems 45 exhibit high polarisability. This property determines their wide application in non-linear optics.^{33-37, 189-193}

Due to considerable changes in the dipole moment, these local transitions are very sensitive to the polarity of the solvent.^{236-238, 241, 242} A decrease in the energy of charge transfer transitions can originate from the rotation of fragments of the molecule in the excited state with the violation of conjugation, for example, of dimethylamino group. In this case, in very polar solvents, fluorescence with an anomalously high Stokes shift and low quantum yield is observed.^{39, 236-238}

Hence, local transitions can influence substantially the spectra of LCS changing even the nature of the longwave band, which usually determines the colour of the compound.

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^a — *Quantum. Electron. (Engl. Transl.)*

^b — *Theor. Exp. Chem. (Engl. Transl.)*

^c — *J. Struct. Chem. (Engl. Transl.)*

^d — *Chem. Heterocycl. Comp. (Engl. Transl.)*

^e — *Opt. Spectrosc. (Engl. Transl.)*

^f — *Russ. J. Org. Chem. (Engl. Transl.)*

Complexes of *d* elements with chelate and macrocyclic ligands as promising components of nonsilver photographic systems

O V Mikhailov

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Abstract. Data concerning the most important aspects of the use in the colour photoprocess with diffusional transfer of the image of coordination compounds of *d* elements with nitrogen-, oxygen-, and sulfur-containing chelate and macrocyclic ligands as the 'working material' or the creation of nonsilver photographic images on silver halide light-sensitive materials by means of their additional treatment and also as the active principle of nonsilver light-sensitive systems are treated systematically and discussed. The bibliography includes 235 references.

I. Introduction

A current characteristic feature of modern coordination chemistry is a tendency, together with the constant expansion of the range of compounds investigated, to expand also the regions of their practical application. During the last 10–15 years, the tendency to employ coordination compounds as components of nonsilver photographic systems has arisen. This will promote the replacement of silver by other less expensive readily available chemical compounds.¹

In principle, economies can be achieved in the use of silver in two ways: by employing coordination compounds either as 'carriers' of photographic images on traditional silver halide light-sensitive materials or as components of nonsilver photographic systems sensitive to radiation. It is noteworthy that the first procedure has nowadays become quite common in silver recovery processes, during which dyes, intensely absorbing in the visible region of the spectrum, arise on the silver halide materials together with silver compounds. After the removal of silver-containing compounds from the photographic emulsion, these dyes form nonsilver photographic images.² The best known dyes of this type are organic dyes containing both nitrogen and oxygen.^{2,3} However, the resistance of these dyes to the action of light and corrosive agents in the environment is low, as a result of which the nonsilver photographic images containing them are decolorised comparatively rapidly.⁴ Dyes based on metal chelates and especially on the metallomacrocycles of 3*d* elements with

nitrogen-, nitrogen and oxygen-, and nitrogen and sulfur-containing ligands are free of this disadvantage. There are grounds for the hypothesis that the latter are extremely promising carriers of nonsilver photographic images regardless of whether they have been formed on nonsilver or even on silver halide light-sensitive materials.

Towards the end of the 1980s, extensive data accumulated on the use of metal chelates and metallomacrocycles of *d* elements as carriers of nonsilver photographic images on AgHal photographic materials and as intrinsic light-sensitive components of photographic emulsions. These results have been surveyed by Mikhailov and Polovnyak.⁵ However, during the time elapsed since the publication of this review (almost ten years), quite a few new investigations have been published. Among them, one must differentiate studies devoted to the use of metal chelate and macrocyclic coordination compounds as the 'working material' for the formation of nonsilver images on AgHal photographic materials, as coloured components in silver halide photographic processes with diffusional transfer of the image, and as the 'active principle' of photographic systems.

II. Chelate and macrocyclic coordination compounds as carriers of nonsilver images formed on 'traditional' AgHal photographic materials

It is known^{1,2,4} that up to 30% of the silver contained initially in the given photographic material remains in the silver images produced on AgHal photographic materials after their exposure and subsequent chemical-photographic treatment in accordance with the standard scheme (development plus fixation). Thus the replacement of a silver image by a nonsilver one can afford fairly appreciable additional economies in the use of silver in the chemical-photographic industry and it follows therefore that this problem cannot be ignored. The process involving the transformation of a silver image into a nonsilver one using carriers based on azo- and azomethine dyes has long been known. In principle, this process actually makes it possible to extract silver fully from the treated AgHal photographic material, but the nonsilver images thus obtained are extremely unstable during storage and are readily 'decolorised' by both light and by corrosive agents in the environment.² On the other hand, chelate and macrocyclic coordination compounds of *d* elements are very inert in relation to the action of the above factors⁶ and one may therefore expect that their employment as carriers of nonsilver photographic images would make it possible to store the image for

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a longer time. This factor stimulated the search for technologies involving the transformation of silver images on AgHal photographic materials which could actually lead to the formation of metal complex nonsilver images. Their essential feature reduces to the following. The elemental silver contained in the initial image is transformed into a mixture of compounds of silver(I) (in particular AgHal) and of some other d element on treatment with a specific solution. Next the photographic emulsion containing this kind of 'mixed' image is treated with a solution which converts the silver(I) compound into a water-soluble one, but does not interact with the other component of the 'mixed' image. This results in the formation of a nonsilver photographic image, the carrier of which is the inorganic compound formed previously in the photographic emulsion together with the silver(I) compound. On treatment of the latter with the appropriate solution, specific complex-formation reactions result in the formation of the final metal chelate nonsilver image. The process described usually involves three stages.^{5,7}

1. The bleaching of the silver image formed initially on the AgHal photographic material as a result of the standard chemical-photographic treatment (development plus fixation) accompanied by the deposition in the photographic emulsion of the hexacyanoferrate(II) complex of some kind of $3d$ element. These two processes can usually be combined. For this purpose, the photographic emulsion with the silver image is kept in an aqueous solution containing potassium hexacyanoferrate(III), some kind of hydroxy acid (usually citric, oxalic, or tartaric) and (or) its salt, and a soluble salt of the $3d$ ion (usually chloride or sulfate). However, in certain cases such combination is impossible and the bleaching and deposition of the corresponding hexacyanoferrate(II) have to be carried out in two different solutions — this happens, for example, in the case of $\text{Co}_2[\text{Fe}(\text{CN})_6]$.

2. The fixation of the bleached image, which results in the elimination from the photographic emulsion of the silver(I) compounds formed in the latter after the bleaching stage. This stage is carried out by maintaining the photographic emulsion with the bleached image in an aqueous solution of sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$).

3. The toning of the image which has passed the above two stages, which results in the formation of the metal chelate nonsilver photographic image. This stage is achieved by maintaining the photographic material in a solution containing some kind of chelating organic compounds and alkaline reagents (usually NaOH, KOH, or Na_2CO_3).

The processes occurring in the first two stages are noncatalytic.³ As a consequence of this, when they are carried out exhaustively the amount of the hexacyanoferrate(II) of the $3d$ element formed in the photographic emulsion is determined exclusively by the content of silver in the initial photographic image. The third stage is none other than the complex formation reaction in $3d$ metal hexacyanoferrate gelatin-immobilised matrix systems.^{8,9} The amount of chelate complex formed depends primarily on the concentration of the hexacyanoferrate(II) of the corresponding metal ion in the photographic emulsion and the concentration of the chelating compounds in the 'toning' solution in contact with it. It is therefore natural to expect that the third stage is in fact decisive in the formation of the nonsilver image with carriers comprising chelate and macrocyclic coordination compounds. A factor such as the solubility of the complex formed in the toning stage then becomes important: if it exceeds a certain critical level, the leaching of this complex from the photographic emulsion comprising the treated material becomes possible, which leads to some decomposition of the metal chelate nonsilver image itself.

The process involving the formation of images in the third stage can be described quantitatively in terms of the following relations: $D' = f(\lg H)$, $D' = f(D^{\text{Ag}})$ or $D' = f(c_{\text{F}}, c_{\text{L}}^0, t)$, where D' is the optical density of the metal chelate image obtained after treatment from the initial silver image with an optical density D^{Ag} , H is the level of exposure ensuring, after carrying out the standard

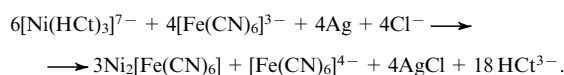
chemical-photographic treatment, the formation of a silver image with a density D^{Ag} , c_{F} is the concentration of the hexacyanoferrate(II) of the corresponding ion of the $3d$ element in the photographic emulsion attained after bleaching and fixation of the silver image, c_{L}^0 is the concentration of the ligand in the solution used in the toning stage, and t is the duration of toning.

The theory of the kinetics of the processes occurring under these conditions and the procedure for the mathematical treatment of the experimental $D' = f(c_{\text{F}}, c_{\text{L}}^0, t)$ relations in order to determine the stoichiometric coefficients of the complex formation reactions and their rate constants have been described by the present author.¹⁰

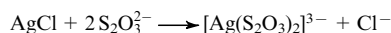
More than 30 different Fe(II), Fe(III), Co(II), Co(III), Ni(II), and Cu(II) coordination compounds with N,O-, N,S-, and N,O,S-chelate and macrocyclic ligands have now been tested for the production of nonsilver photographic images on AgHal photographic materials.^{11–81} The increased attention devoted precisely to the chelates of the above metal ions is linked directly to factors such as the ease of their formation in gelatin emulsions of the AgHal photographic materials, the considerable absorption intensity in the visible part of the spectrum, and a fairly high thermodynamic stability.¹² The carriers for metal chelate nonsilver images mentioned most frequently are Ni(II) chelates,^{13–42} to a lesser extent Cu(II) chelates,^{43–64} and to a still lesser extent Co(II) and Co(III)^{65–75} as well as Fe(II) and Fe(III)^{76–81} chelates. In most cases the formation of metal chelate photographic images proceeds in a very complex manner and the composition of the nonsilver image depends on the concentration-time regime (*i.e.* on the specific values of the parameters c_{F} , c_{L}^0 and t).^{29, 30, 58, 74} However, one should note that in a number of instances, for example in the Ni(II)–8-mercaptoquinoline (or its 5-substituted derivatives),^{31, 39, 40} Ni(II)–*N,N'*-diphenyldithiooxamide,^{19, 29, 30} Fe(II)–isonitrosoacetone,⁷⁷ and Fe(II)–8-mercaptoquinoline⁷⁸ systems, the formation of only one complex species with metal ion:ligand ratios of 1:2, 1:2, 1:2, and 1:3 respectively was recorded.

The formation of nonsilver images from chelate and macrocyclic Ni(II) coordination compounds is preceded by the stage involving the bleaching of the silver image with deposition of $\text{Ni}_2[\text{Fe}(\text{CN})_6]$. In all the cases described in the literature, this stage is carried out using the following composition: 15.0 g $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ + 88.0 g Na_3HCT (or K_3HCT) + 14.0 g $\text{K}_3[\text{Fe}(\text{CN})_6] + \text{H}_2\text{O}$ (up to 1 litre) [HCT^{3-} is the citrate trianion $-\text{O}_2\text{CCH}(\text{OH})\text{CH}(\text{CO}_2^-)\text{CO}_2^-$].

The bleaching stage is usually carried out for 20–25 min at 20–25 °C. Nickel hexacyanoferrate is formed by the reaction

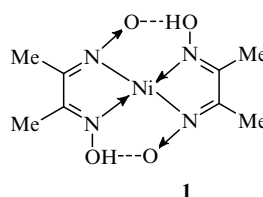


After the 'bleaching' of the image



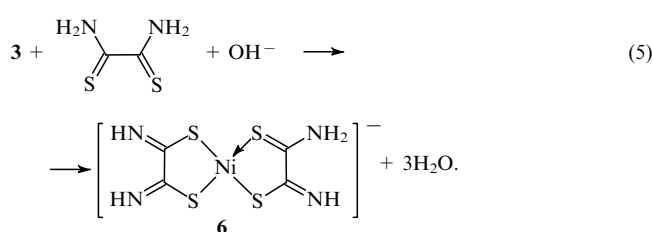
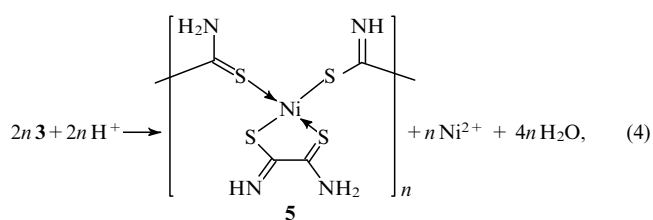
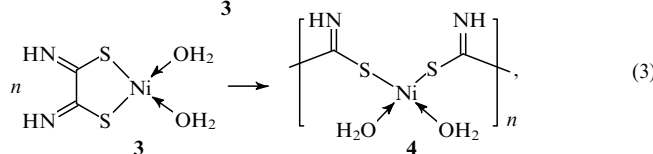
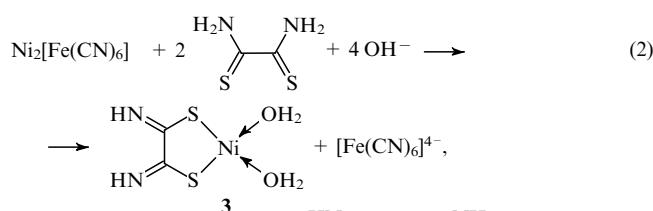
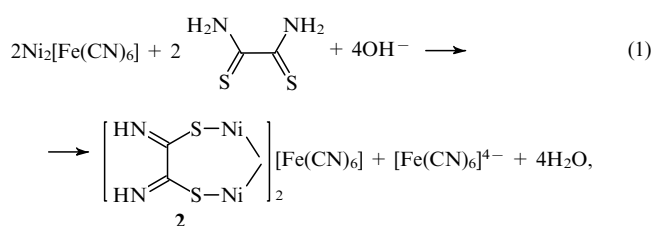
only nickel hexacyanoferrate remains in the photographic emulsion imparting a pale yellow-green colour to the latter. By varying further the composition of the toning solution under toning conditions, it is possible to obtain diverse nickel-containing nonsilver photographic images.^{11, 12}

The most familiar coordination compound which may be used to form a nonsilver photographic image on AgHal light-sensitive materials is bis(dimethylglyoximate)nickel(II).⁸²



The generation of images with this type of carrier has been described.^{11, 12, 15, 16} It was noted that the optical density relations $D' = f(\lg H)$, $D' = f(D^{Ag})$, and $D' = f(c_F, c_L^0, t)$ put forward above are monotonic, lack extrema, and tend to a limiting value with increase in c_L^0 and t for a fixed value of D^{Ag} (and hence c_F). The nonsilver pink or pink-red images obtained are of particular practical interest because, when they are examined under green light (to which the eye is known to be most sensitive), there is an appreciable increment in the optical densities D compared with the optical densities of the initial silver image D^{Ag} .^{15, 16}

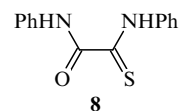
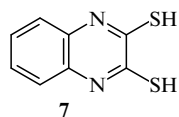
The formation of nonsilver images based on Ni(II) chelates comprising dithiooxamide has been investigated in detail because of the extremely interesting colour transitions occurring in this instance and the wide variety of coordination compounds produced.^{8, 11, 12, 14, 21, 22, 29, 30, 32–34} On interaction of nickel(II) hexacyanoferrate, formed in the photographic emulsion after the occurrence of stages 1 and 2, solutions of dithiooxamide (pH 12.0) give rise to five different complexes **2–6**.^{8, 29, 30, 32–34}



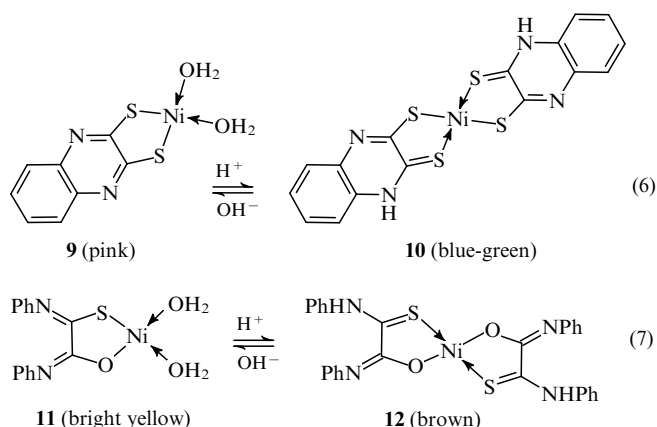
Compounds **2–5** are insoluble in water and impart a greenish-blue colour to the photographic emulsion with a grey tint ($\lambda_{\text{max}} = 590\text{--}610$ nm), a pink-violet colour ($\lambda_{\text{max}} = 580$ nm), a violet colour ($\lambda_{\text{max}} = 570$ nm), and a dark-blue colour ($\lambda_{\text{max}} = 640$ nm) respectively, while compound **6**, being insoluble in water, readily diffuses from the photographic emulsion into the toning solution in contact with the latter. A unique and from the practical point of view an extremely valuable property is actually associated with the formation of compound **6**: the process involving the generation of non silver images from nickel(II) chelate complexes of dithiooxamide at fairly high concentrations of the

above organic reagent in the toning solution (8.0×10^{-3} M) is not only unaccompanied by an increase in fogging compared with that for the initial silver image but actually entails its diminution. (At dithiooxamide concentration in the toning solution $c_L^0 > 0.1$ M, the nonsilver image is not formed at all.²⁹) This factor has been used at one time to increase the sensitivity of direct positive photographic materials.²⁶ In an early study,¹⁴ it was noted that the process involving the generation of such images may be applied successfully to prepare the so-called blue slides, which have been recently used increasingly for presenting illustrations at conferences, symposia, *etc.* The preparation of 'blue slides' with carriers consisting of nickel(II) chelate complexes of dithiooxamide has been investigated in detail.^{21, 22, 29} It has been noted that this process is less laborious and, which is particularly important, its sensitivity to external conditions is much less critical compared with the traditional technology for the preparation of 'blue slides' on the basis of organic dyes, one of the versions of which has been described by Filin *et al.*⁸³ The fact that the sky-blue or blue metal chelate images obtained in our case have a higher purity of their light lines and a better contrast than those described by Filin *et al.*⁸³ merits attention in this connection. It is remarkable that none of the processes (1)–(3) in the nickel(II)–dithiooxamide system has been recorded hitherto for complex formation in solution.^{32, 33}

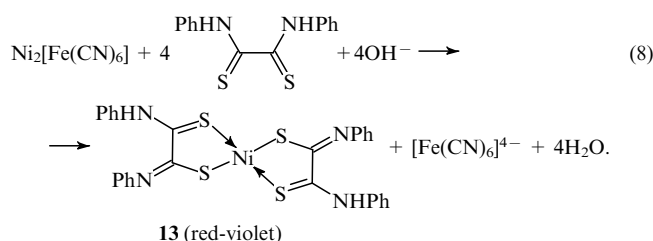
Bearing in mind the set of formation reactions of compounds **2–6**, it is easy to explain the unusual time variation of the optical densities of the nonsilver image in the third stage: for $c_L^0 > 8.0 \times 10^{-1}$ M, the values of D' initially increase with t , reach a maximum, and then fall.^{11, 12, 29, 30} According to Eqn (4), the transition **4** $\rightarrow$ **5**, entailing a change in the colour of the photographic emulsion from violet to dark-blue, is possible in an acid medium. The concluding stage of the technological process for the preparation of 'blue slides' is associated with this transition.^{14, 26, 29, 30} A similar type of $D' = f(D^{Ag})$ and $D' = f(c_F, c_L^0, t)$ relations has also been noted for the processes involving the generation of nonsilver photographic images with carriers consisting of nickel(II) chelate complexes of quinoxaline-2,3-dithiol **7** and *N,N'*-diphenylthiooxamide **8**.^{19, 28, 35}



Incidentally, here too the transition from chelates with complete deprotonation of the ligands to chelates with partial deprotonation of the latter is also observed, which is accompanied by a sharp alteration in the colour of the metal chelate photographic image (from pink to blue-green in the case of quinoxaline-2,3-dithiol and from bright-yellow to brown in the case of *N,N'*-diphenylthiooxamide).^{29, 35, 37} It is remarkable that, in contrast to the process in which a dark-blue nonsilver image is generated from the nickel(II) chelate complex of dithiooxamide (the transition **4** $\rightarrow$ **5**), the analogous processes involving the generation of blue-green and brown images from quinoxaline-2,3-dithiol and *N,N'*-diphenylthiooxamide are reversible and, when they are treated with alkaline solutions at pH > 9.0 , their initial colour (pink and bright-yellow respectively) is immediately restored^{35–37} and a very appreciable decrease (to the extent of 50%–55%) in the optical densities of both the pink and bright-yellow metal chelate images is then observed. Whereas complex **5** is a coordination polymer, the nickel(II) complexes of quinoxaline-2,3-dithiol and *N,N'*-diphenylthiooxamide are coordination monomers because steric hindrance in the quinoxaline-2,3-dithiol and *N,N'*-diphenylthiooxamide molecules precludes the formation of polymeric compounds. The processes involving the generation of metal chelate images can therefore be described by reactions (6) and (7) in the case of quinoxaline-2,3-dithiol and *N,N'*-diphenylthiooxamide.

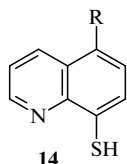


Reactions (1)–(7) do not occur on formation of nonsilver metal chelate images from nickel(II) coordination compounds with a ligand close to dithiooxamide and *N,N'*-diphenylthiooxamide — *N,N'*-diphenyldithiooxamide PhNHC(S)C(S)NPh ; in this case, this process is described by Eqn (8):³⁵



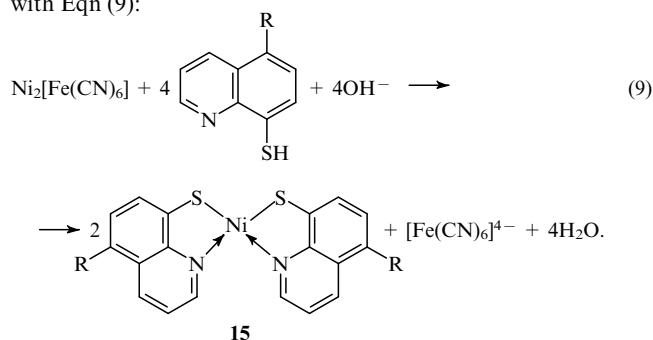
The cause of this difference should be sought both in the influence of diffusion factors and in the poor proton-donating properties and the sparing solubility of *N,N'*-diphenyldithiooxamide compared with dithiooxamide and *N,N'*-diphenylthiooxamide.

The technology for the generation of nonsilver photographic images from nickel(II) chelate complexes of 8-mercaptoquinoline and a series of 5-substituted derivatives having the general formula **14** has been described.^{23, 24, 32, 38–40}



R = H, SH, SMe, Cl, Br.

In this case, the nonsilver image is generated in accordance with Eqn (9):



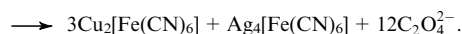
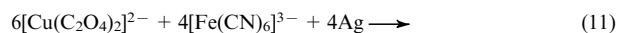
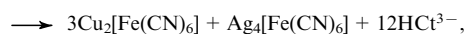
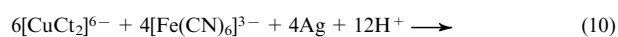
The colour of the images thus obtained varies from pink-red to dark-brown. A very steep slope of the $D' = f(D^{\text{Ag}})$ curves in the range of low optical densities of the initial silver image is

characteristic of the nickel(II) complexes of unsubstituted 8-mercaptoquinoline. It has been suggested that this factor be used to intensify very weak photographic images on radiographic materials.^{31, 39} A very considerable increase in D' compared with D^{Ag} has been noted also for nonsilver metal chelate images based on nickel(II) compounds of 5-chloro-8-mercaptoquinoline.^{38, 40}

The nonsilver images derived from copper(II) chelate complexes with N,O-, N,S-, N,O,S-, and S,S-donor ligands are also of interest. Their absorption in the visible region of the spectrum exceeds in most cases the absorption of the analogous nickel(II) chelates. Formally this fact renders copper(II) coordination preferable for the generation of nonsilver metal chelate photographic images compared with those based on nickel(II). This probably accounts for the greater range of copper(II) chelate complexes compared with the nickel(II) complexes.¹²

The formation of metal chelate images is also preceded by the stage in which the initial silver images is bleached and fixed. The bleaching is carried out either in the 7 g $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} + 90$ g Na_3HCT (or K_3HCT) + 6 g $\text{K}_3\text{Fe}(\text{CN})_6 + \text{H}_2\text{O}$ (up to 1 litre) solution (see Mikhailov and Polovnyak⁵³) or the 7 g $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} + 50$ g $\text{K}_2\text{C}_2\text{O}_4 + 4$ g $\text{K}_3\text{Fe}(\text{CN})_6 + \text{H}_2\text{O}$ (up to 1 litre) solution (see Mikhailov *et al.*⁶²).

In both cases, the bleaching process occurs at 20–25 °C for 20 min. The nonsilver image generation processes are described by Eqns (10) and (11):

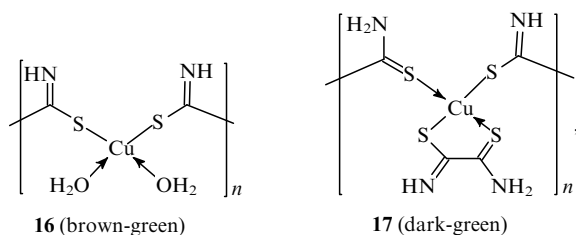


In order to fix the 'bleached' image, the treatment of the latter in aqueous $\text{Na}_2\text{S}_2\text{O}_3$ solutions for 3–5 min is used as in the case of $\text{Ni}_2[\text{Fe}(\text{CN})_6]$; the process occurring under these conditions is described by the equation



After bleaching and fixation, copper(II) hexacyanoferrate remains in the photographic emulsion, imparting a red or red-brown colour to the photographic image. The optical densities of this intermediate nonsilver image are fairly high and, when it is observed through a blue light filter, they actually exceed the densities of the initial silver image.^{11, 12} There are data showing that the bleaching with the 'copper hexacyanoferrate oxalate' bleaching agent affords higher optical densities of the intermediate metal hexacyanoferrate image than bleaching with the 'copper hexacyanoferrate citrate' bleaching agent.⁸⁴ The reason for this difference has not so far been elucidated, but it is undoubtedly not in any way related to the difference between the covering powers of the $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ constituting this image because subsequently, during toning under identical conditions, the optical densities of the metal chelate nonsilver images obtained are found to be different. Presumably, in the case of the 'copper hexacyanoferrate citrate' bleaching agent the $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ formed during bleaching dissolves to a slight extent, whereas in the case of the 'copper hexacyanoferrate oxalate' bleaching agent the dissolution does not occur at all or its extent is much smaller because the citrate anion forms more stable coordination compounds with copper(II) than does oxalate.⁸⁵

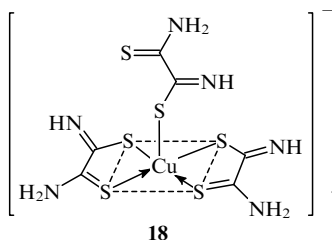
The formation of nonsilver images from copper(II) coordination compounds of dithiooxamide has been most thoroughly investigated.^{44, 53, 60, 61} According to the results of a number of investigations^{44, 53, 60, 61}, when the photographic emulsion containing $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ comes into contact with an alkaline ($\text{pH} \approx 12$) solution of dithiooxamide, the water-insoluble coordination polymers



are formed. They are structurally analogous to polymers **4** and **5** and the polymeric copper(II) hydroxide. The last compound arises as a result of the alkaline degradation of $\text{Cu}_2[\text{Fe}(\text{CN})_6]$:

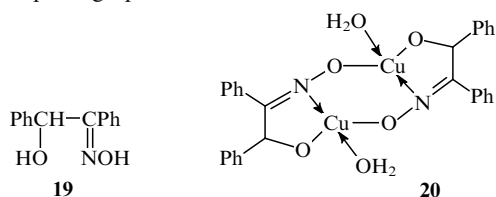


It is noteworthy that copper hydroxide accumulates in appreciable amounts in the gelatin emulsion of the treated photographic material only at extremely low ($<10^{-5}$ M) concentrations of dithiooxamide in the toning solution in contact with this material.⁶¹ The optical densities D' of the nonsilver images based on the copper(II) complex of dithiooxamide are appreciably higher than the optical densities of the images based on nickel(II) chelates (cf the studies described in Refs 29 and 30, on the one hand, and that in Ref. 53, on the other). However, the image based on copper(II) chelate complexes of dithiooxamide also decomposes readily at fairly high ligand concentrations in the toning solution ($\sim 1.5 \times 10^{-2}$ M), like the image based on nickel(II) chelates, as a consequence of the formation of soluble 1:3 complex **18**, to which the following structure has been attributed:

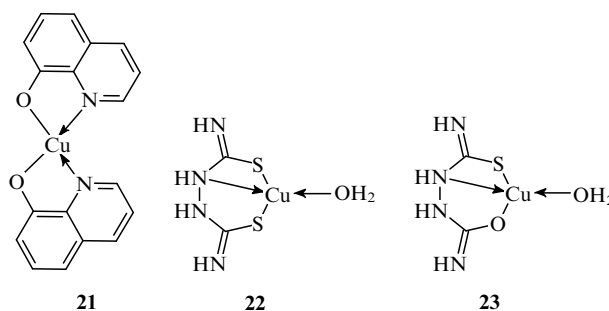


This factor should lead to the appearance of maxima on the $D' = f(c_F, c_L^0, t)$ curves.^{60,61} The difference between the shapes of the kinetic curves in the nickel(II)–dithiooxamide and copper(II)–dithiooxamide systems consists only in the fact that the degradation of the copper(II) chelate image begins at higher ligand concentrations in the toning solution than the degradation of the nickel(II) chelate complex of dithiooxamide.

Complexes with analogous compositions and structures are formed also in the course of the generation of nonsilver images from copper(II) chelate complexes of quinoxaline-2,3-dithiol.^{45,60} According to the present author's data,⁶⁰ dimeric copper(II) chelate complexes with the above ligand have the 2:2 and 2:4 compositions (depending on the degree of deprotonation of the ligand). Nonsilver images based on copper(II) chelate complexes of α -benzoin oxime **19**, distinguished by a very high resolving capacity, not inferior to that of the initial silver image, have also been described in the literature.^{46,86} Judging from all the available evidence, in this case the dimeric bright-green chelate **20** is formed in the photographic emulsion.

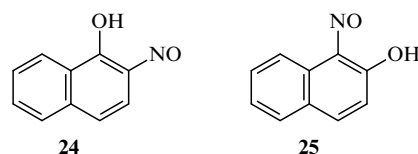


The copper(II) complexes of 8-hydroxyquinoline (the bright-green complex **21**),⁴⁸ 8-mercaptoquinoline, bis(thiocarbamoyl)hydrazine (the black complex **22**), and 1-carbamoyl-2-thiocarbamoylhydrazine (the black-brown complex **23**) have also been described.^{50,60,62}

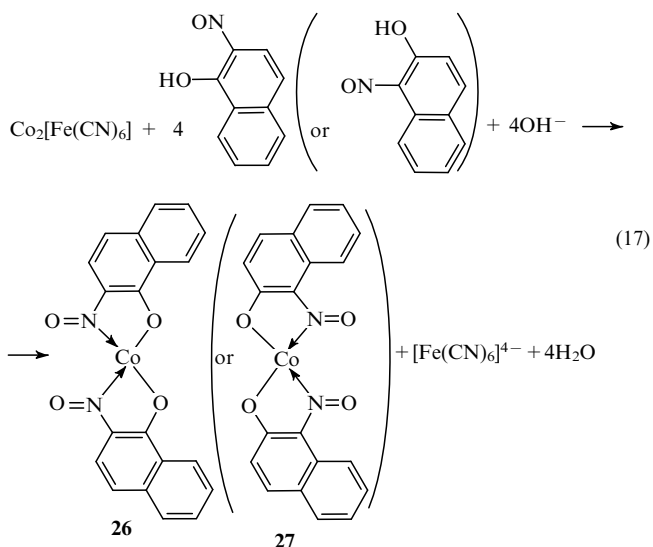
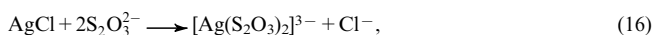
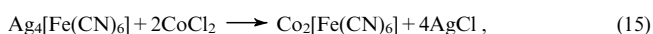


In the last two cases, nonsilver photographic images are obtained, the colour and optical characteristics of which are extremely close to those of the initial silver image. Several studies have been devoted to the nonsilver images based on copper(II) chelate complexes of various 3-benzoylthioureas $\text{RHN}-\text{C}(\text{S})-\text{NH}-\text{C}(\text{O})\text{Ph}$, where R is an aryl group with bulky substituents.^{55–59} In most cases, the photographic images have colours with 'warm' tones, the tints of which are determined both by the nature of the chelating agent and the concentration-time regime in the toning stage.^{7,8,60}

Only two cobalt(II) coordination compounds used as carriers of nonsilver photographic images are known at present, namely the chelate complexes of 2-nitroso-1-naphthol **24**^{65,71,73} and the isomeric 1-nitroso-2-naphthol **25**.⁷³

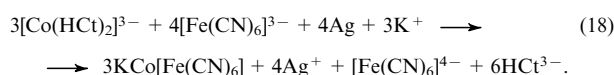


According to the literature,^{65,71,73} these images are formed in four stages: bleaching [4% aqueous $\text{K}_3\text{Fe}(\text{CN})_6$ solution, 10–12 min, 20–25 °C]; intermediate toning (5% aqueous CoCl_2 solution, 10 min, 20 °C); fixation (25% aqueous $\text{Na}_2\text{S}_2\text{O}_3$ solution, 3–5 min, 20–25 °C); generation of the nonsilver image (1–10 min, 20 °C). The first three stages correspond to the generation of the intermediate image. The process occurring under these conditions are described by Eqns (14)–(17) respectively:



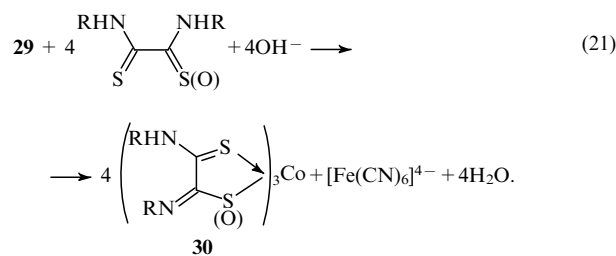
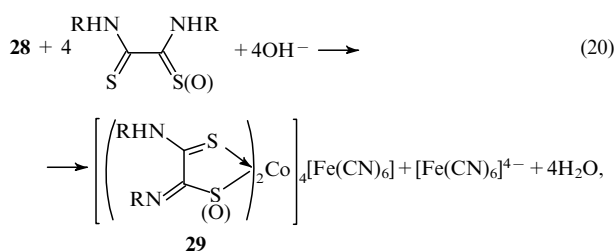
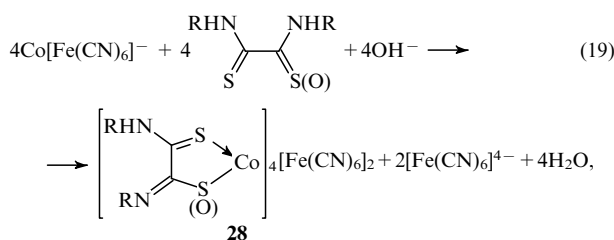
The intermediate image obtained on $\text{Co}_2[\text{Fe}(\text{CN})_6]$ has a pale-green colour, whereas the images based on the chelates **26** and **27** have dark-red and brick-red colours respectively^{65, 71, 73} with extremely high optical densities in green and blue light. With increase in the duration of the fourth stage (toning) and also with increase in the concentrations of both isomeric nitrosonaphthols in the toning solution, the densities D' increase monotonically, tending to certain limiting values.⁷³

Despite the fact that cobalt(III) forms a much greater number of coordination compounds with chelating and macrocyclic N,O-, N,S-, and N,O,S-donor ligands compared with cobalt(II), only very few of them have been used as carriers of photographic nonsilver images.^{66–70, 72, 74} The synthesis of nonsilver images based on cobalt(III) chelates from initial silver images can be achieved in three stages. The first two correspond to the formation in the photographic emulsion of an intermediate image from cobalt(III) hexacyanoferrate, whilst the third corresponds to the formation of the target metal chelate image. Bleaching is carried out in the course of 20–25 min at 20–25 °C in the 10 g $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ + 50 g Na_3HCT (or K_3HCT) + 4 g H_4Ct + 4 g $\text{K}_3\text{Fe}(\text{CN})_6$ + 0.2 g L-methionine + H_2O (up to 1 litre) solution. Fixation is carried out in 25% $\text{Na}_2\text{S}_2\text{O}_3$ solution at 20–25 °C for 3–5 min. According to literature data,^{66, 70, 74} the processes occurring under these conditions can be described by Eqns (18) and (16) respectively:



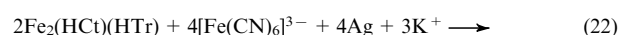
The optical densities of the intermediate nonsilver image thus obtained, measured through blue, green, and yellow light filters, greatly exceed the optical densities of the initial silver image.⁸⁴ It is interesting to note that the $D' = f(D^{\text{Ag}})$ relations for such images on negative phototechnical films have a distinct maximum,^{84, 87} whereas on radiographic films there is no such maximum. This difference was attributed⁸⁷ to the different degrees of graininess of the photographic emulsions comprising the materials indicated.

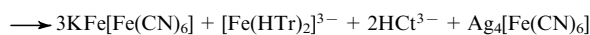
The processes leading to the formation of nonsilver images from cobalt(III) chelates have been analysed in greatest detail in a study by the present author,⁷⁴ who noted, in particular, extremely complex $D' = f(D^{\text{Ag}})$ relations on formation of images with carriers comprising cobalt(III) chelate complexes with ligands such as dithiooxamide, N,N' -diphenyldithiooxamide, and N,N' -diphenylthiooxamide. According to the present author,⁷⁴ this form of the curves may be fairly adequately interpreted in terms of the concept of stepwise complex formation in accordance with Eqns (19)–(21):



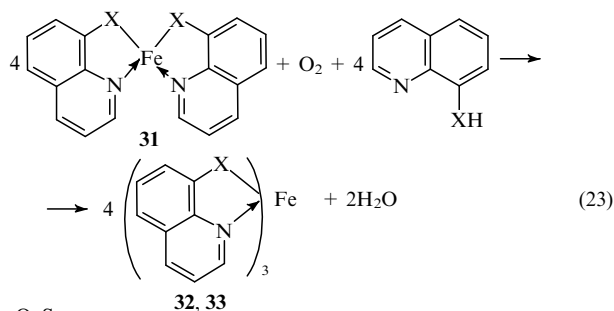
It is noteworthy that, in contrast to the nickel(II) and copper(II) chelates, in the generation of nonsilver images from cobalt(III) chelate complexes of dithiooxamide a dependence of the nature of the $D' = f(\lg H)$ and $D' = f(D^{\text{Ag}})$ curves on the type of photographic material in which the initial silver image had been formed is observed. Thus, in the case of radiographic or direct positive films, these curves have a single maximum,^{66, 74} whilst in the case of negative phototechnical films there are two maxima,^{66, 70} the first of which corresponds to the maximum observed on these photographic materials for intermediate cobalt(III) hexacyanoferrate images, while the second is located in the region of lower values of $D^{\text{Ag}}(\lg H)$. It is even more remarkable that the second maximum is observed only in measurements through a blue light filter.⁶⁶ Another characteristic feature is that, immediately after the attainment of the second maximum, there is a sharp alteration of the colour of the image from amber-yellow to brick-red, which is linked directly to processes (20) and (21).^{66, 70, 74} This type of $D' = f(D^{\text{Ag}})$ relations is entirely unique and has no analogues whatever among other nonsilver photographic image generation processes. It must be specially emphasised that the nonsilver images considered exhibit a very high absorption in the visible part of the spectrum, as a result of which the photographic sensitivity of the treated AgHal material may increase during their formation by a factor of 30–50 and more compared with that for the initial silver image,^{72, 74} which is of undoubted practical interest. Nonsilver photographic images based on cobalt(III) chelate complexes of 8-mercaptoquinoline, which, like the images based on cobalt(III) chelate complexes of dithiooxamide and its analogues, have a dark-brown colour, have been described;⁶⁹ however, these images have not so far been investigated.

Iron(II) or iron(III) chelate complexes should be of greatest interest as 'working materials' for nonsilver images based on coordination compounds of 3d elements because iron and its compounds are cheapest and most readily available. Unfortunately, the majority of iron(II) and iron(III) complexes are relatively unsuitable for the generation of nonsilver photographic images because of their weak absorption in the visible part of the spectrum and appreciable solubility in water. For this reason, the list of iron coordination compounds used as carriers for nonsilver images is extremely limited. Only images based on iron(II) chelate complexes of 8-hydroxyquinoline^{76, 79, 81} and isonitrosoacetone⁷⁷ [the 'iron(II) ion:singly deprotonated form of ligand' ratio is 1:20] and iron(III) chelate complexes of 8-mercaptoquinoline (the above ratio is 1:3)⁷⁸ have been described in the literature. Such images are obtained in three stages: (1) bleaching in the 5 g NH_4FeCt + 2.0 g H_4Tr (H_4Tr = tartaric acid) + 4.5 g $\text{K}_3\text{Fe}(\text{CN})_6$ + 2.5 g $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ + H_2O (up to 1 litre) solution (see Mikhailov and Budnikov⁷⁸) or the 5 g NH_4FeCt + 1.8 g H_4Tr + 4.0 g $\text{K}_3\text{Fe}(\text{CN})_6$ + 0.1 g $\text{K}_2\text{Cr}_2\text{O}_7$ + H_2O (up to 1 litre) solution (see Mikhailov and Polovnyak⁷⁷); (2) fixation in 25% aqueous $\text{Na}_2\text{S}_2\text{O}_3$ solutions; (3) transformation of the intermediate image arising in the bleaching stage into the metal chelate image. The intermediate image is coloured sky-blue or blue and has an extremely high optical density in red light.⁸⁴ It could have full independent practical importance were it not for its low resistance to photodegradation by UV and visible light and also by alkaline agents. The generation of this image can be described by Eqns (12) and (22):





The most promising ligand for the generation of photographic iron chelate images is 8-hydroxyquinoline, which forms the dark-brown compound **31** with iron(II). It imparts to the gelatin emulsion of the photographic material a colour which is very close to that of the initial silver image but with higher optical densities.⁷⁹ In the course of the formation of nonsilver images with such a carrier, compound **32** is formed simultaneously (in a small amount).^{76, 79}



This reaction was not detected in the formation of nonsilver images from iron(II) chelate complexes of isonitrosoacetone (which are coloured blue).⁷⁷ However, the oxidation-reduction reaction (23) is decisive in the formation of nonsilver images from the iron chelate complexes of 8-mercaptoquinoline (coloured orange). According to Mikhailov and Budnikov,⁷⁸ the emulsions contain exclusively tris(8-mercaptoquinolinato)iron(III) **33**, while bis(8-mercaptoquinolinato)iron(II) was not detected in the photographic emulsion in appreciable amounts of any kind.

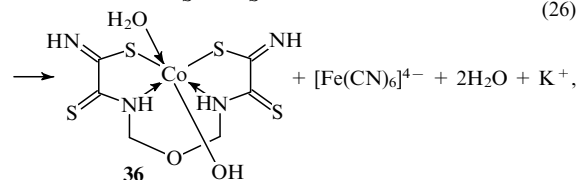
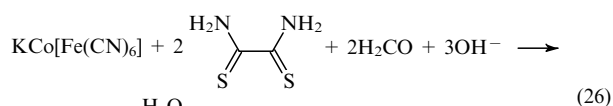
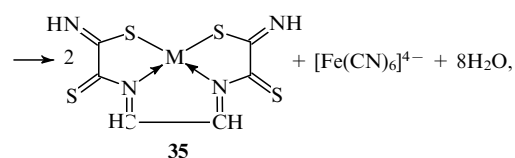
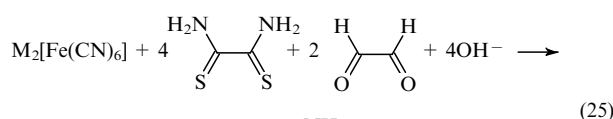
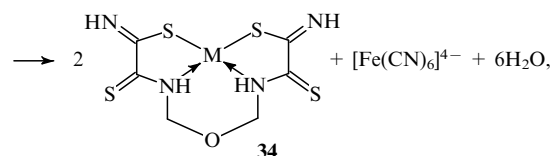
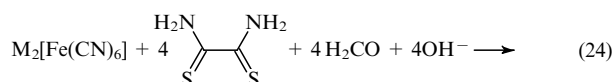
Summarising, one should note that the concrete result of the transformation of the silver image into the metal chelate nonsilver image — intensification or attenuation compared with the initial silver image — depends significantly not only on the nature of the chelate complex constituting the image and the concentration — time regime in the toning process but also on the type of photographic material. It has been noted that intensification of the image is usually observed on the photographic emulsions of radiographic AgHal materials, whereas the image is actually attenuated in the photographic emulsions of negative phototechnical and direct positive films.^{13–20, 43–51, 65–67} This factor has been attributed to the greater 'covering power' (the ratio of the optical density of the image and the concentration of the carrier present in it) of silver in images on the last two types of photographic materials, as a consequence of which lower concentrations of silver in the initial image correspond to the same optical density in the case of phototechnical and direct positive films compared with the concentration in the case of radiographic films, as a result of which smaller amounts of the hexacyanoferrate(II) of the corresponding metal are deposited together with the silver(I) compounds in the course of bleaching.

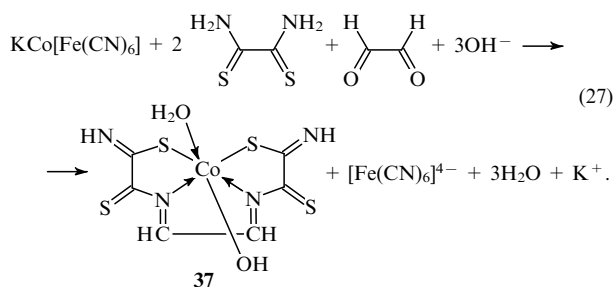
It is noteworthy that in a number of instances the nonsilver images on AgHal photographic materials may be obtained by means of a short procedure: for this purpose, the initially exposed photographic material is developed and is then immediately treated without fixation (the fixation stages have been used in some studies^{11–81}) by the procedure described above involving the transformation of the silver image into a metal chelate nonsilver image. Despite the shortening of the overall duration of the treatment, it is then possible to accelerate and render more complete the bleaching of the silver formed in the photographic emulsion after the development stage. However, this possibility has been indicated only in patent publications.^{88–92}

Mikhailov and Polovnyak⁸⁶ measured certain quantitative structural characteristics of metal chelate nonsilver images and in particular their resolving power. These measurements demonstrated that in most cases the given parameters differ extremely little from the analogous parameters for the initial silver image.

This indicates the possibility of employing such images even for defectoscopic purposes, in particular in medical radiography. The data on the resolving power of nonsilver images based on copper(II) chelate complexes of α -benzoin oxime⁸⁶ give grounds for the hope that the carriers entering into their composition may be recommended for the generation of images on holographic materials, where the most severe requirements must be met by the resolving capacity of photographic materials.¹ It is striking that the decrease in the resolving power of nonsilver metal chelate images compared with that of the initial silver image has been noted predominantly in those cases where the chelate constituting the image undergoes partial degradation during complex formation as a consequence of its deprotonation or the attachment of additional ligand molecules, which is accompanied by the formation of soluble complexes.⁸⁶

Data have recently appeared in the literature concerning the possibility of obtaining nonsilver photographic images consisting of coordination compounds of *d* elements with macrocyclic ligands during their so called mild template synthesis in metal hexacyanoferrate gelatin-immobilised matrix systems.^{41, 42, 63, 64, 93–95} The carriers for such nonsilver images are cobalt(III), nickel(II), and copper(II) coordination compounds of 2,8-dithiono-3,7-diaza-5-oxanonane-1,9-dithioamide and 2,7-dithiono-3,6-diazaocta-3,5-diene-1,8-dithioamide (complexes **34–37**), arising when photographic emulsions containing cobalt, nickel, and copper hexacyanoferrates come into contact with dithiooxamide — formaldehyde or dithiooxamide — glyoxal toning solutions. According to the literature,^{41, 42, 63, 64, 93–95} the following reactions occur in this case:





The generation on AgHal photographic materials of nonsilver images with carriers of this kind makes it possible to achieve an appreciable increase in photographic sensitivity (almost by two orders of magnitude) compared with that for the initial silver image.^{64, 93–95} Judging from the literature data,^{41, 42, 63, 64, 93–95} the use of template synthesis reactions gives rise to new possibilities for the synthesis of metal chelate nonsilver images and large scale studies are clearly necessary in this field.

There are indications of the possibility of obtaining polychromic metal chelate nonsilver images in which the nickel(II) coordination compounds of *N,N'*-diphenylthioxamide, dimethylglyoxime, and dithioxamide, already mentioned, serve as the yellow, purple, and sky-blue components, although unfortunately this possibility has not so far been realised in practice.⁹⁶

III. Metal chelates and metallomacrocycles in the colour photographic process with diffusional transfer of the image

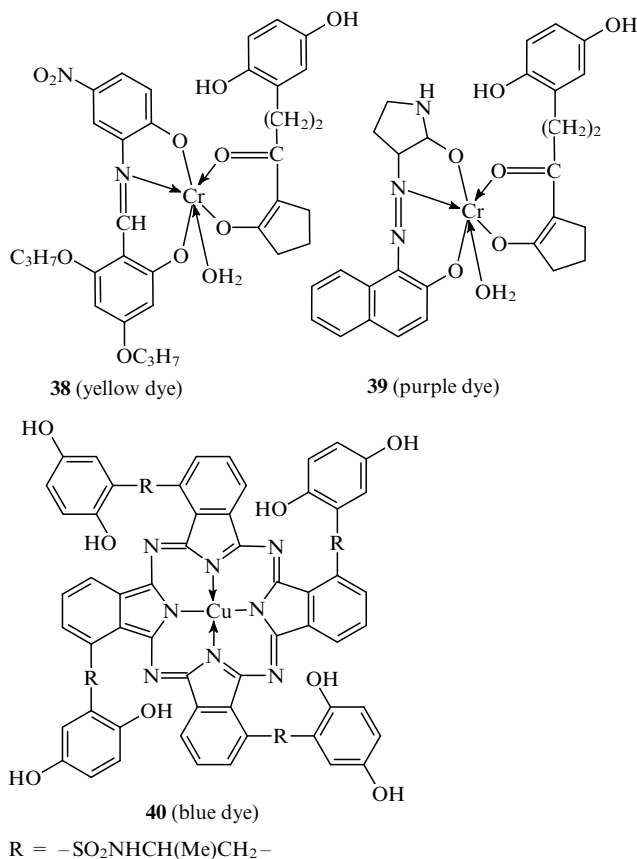
In the photographic processes examined in Section II, the nonsilver photographic images with metal chelate carriers arose in the photographic emulsion of the initial AgHal photographic material as a result of the transformation of the silver image produced on it initially into the nonsilver target image via a series of specific chemical reactions. The individual stages of the process leading to the transformation of the silver image into the nonsilver one were then separated both in space and in time. However, it is possible to imagine a AgHal photographic system in which these metal chelates or their derivatives are already present initially in a 'pure form' whereupon the nonsilver image is formed in one stage. This version of the single-step AgHal process, in which exposure and the chemical-photographic treatment take place simultaneously, was proposed in 1947 by the American inventor E Land.⁹⁷ In the process which he proposed, the light-sensitive emulsion of the exposed photographic material immediately came into contact with photographic paper containing a special layer of varnish. In the course of the chemical-photographic treatment, particles of the metal chelate dye, creating a negative image in the photographic material, remained on the exposed sections, whereas the particles of the dye remaining on the unexposed sites of the photographic material diffused into the receiving layer of the photographic material on an opaque support (usually photographic paper), where the positive coloured image was in fact created.

In the photographic process with diffusional transfer of the image, photographic materials consisting of three layers are usually employed.

Each of them is in its turn divided into two sublayers: the upper light-sensitive layer containing AgHal and reacting selectively to red, green, or blue light and the lower layer with an intensely coloured metal chelate, the colour of which is 'complementary' to that of the zonal sensitivity of the upper sublayer (namely sky-blue, purple, and yellow). The nonsilver image consists of a mixture of the above dyes, the ratio of which in the ultimate image depends primarily on the level of exposure and the spectral composition of the exposing radiation, so that the image is almost always polychromic. The carriers of these images are

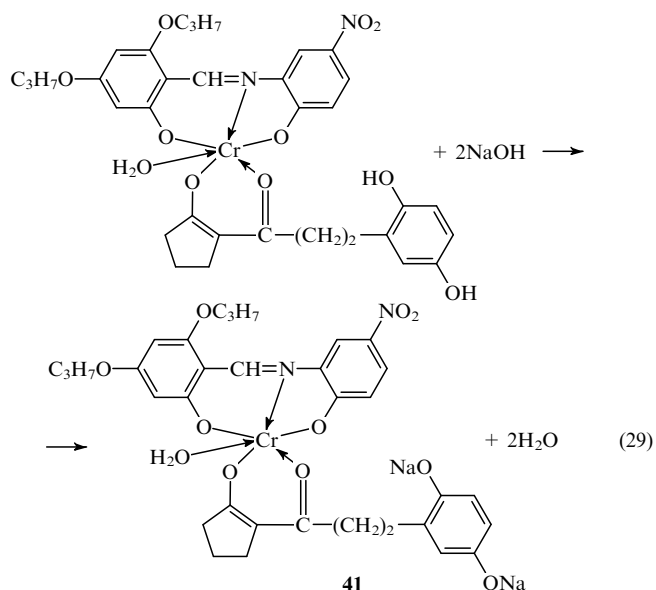
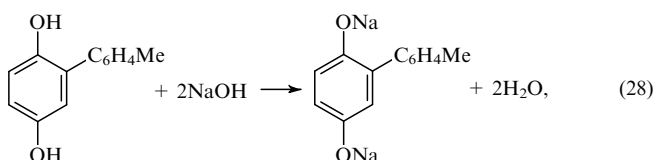
usually none other than intensely coloured coordination compounds of 3d elements with N-, N,O-, or N,S-containing chelating or macrocyclic ligands.^{98–137} This type of AgHal photographic process has been called a colour diffusion photographic process; several reviews have been devoted to it.^{106, 110, 138–140}

At the present time the most popular is the AgHal photographic process where the purple and yellow colouring components are chromium(III) coordination compounds of azomethine dyes or azo-dyes, while the sky-blue component is a copper(II) chelate complex of the macrocyclic phthalocyanine formed in the course of template synthesis.^{98–109} Thus the chelates **38–40** have been used.¹⁰¹ The SX-70 Polaroid photographic material with diffusional transfer of the photographic image (USA) is widely known. Dyes of the above or similar composition are used in it as the colour components.¹⁰⁵ Judging from all the available evidence, the combination of the chelate complexes **38–40** is altogether one of the most successful.

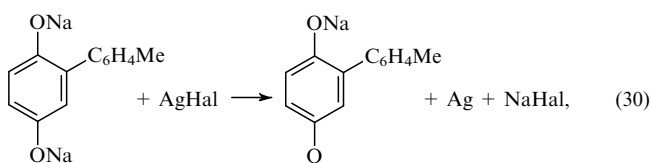


Other chromium(III) coordination compounds have also been proposed as reagents for the generation of nonsilver metal chelate images, but, so far as we are aware, they have not found any kind of appreciable practical use.

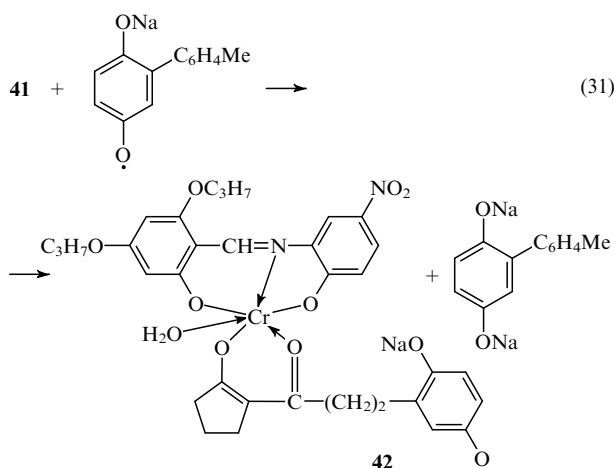
The nonsilver image formation processes in the colour diffusion photographic process have been described in detail.^{106, 110} For chemical photographic treatment of photographic materials with diffusional transfer of the photographic image, use is made of compositions an obligatory element and active principle of which is NaOH, KOH, or another alkaline agent. Diffusing in the course of the photographic treatment in the light-sensitive layer, the alkaline agent ionises the developing substance present in the photographic emulsion (this is usually methylphenylhydroquinone, which performs the same function in this instance as in the standard AgHal photographic process) and the colouring components. An example of the ionisation of a yellow dye is presented below:



On the exposed regions, sodium (or potassium) methylphenylhydroquinonate reduces AgHal [Eqn (30)], being converted at the same time into the corresponding radical-ion:



By subtracting an electron from the ionised form of the dye, the radical-ion transforms it into the semiquinone form. A scheme illustrating the formation of semiquinones for a yellow dye is presented below:

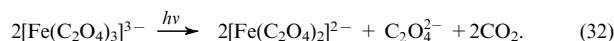


The semiquinones are fairly readily converted into insoluble dyes, incapable of diffusion and not coming into contact with the reception layer. On the unexposed sections of the photographic material, where the semiquinones are not formed, the soluble forms of the colouring components (the ionised forms) permeate into the reception layer and come into contact with the photographic paper, being at the same time reconverted into the insoluble forms. A nonsilver metal chelate image is formed on the photographic paper as a result.

Apart from the coordination compounds **38–40**, there is of course a possibility of using also other representatives of complexes of the given class. Thus it has been suggested that cobalt(II) and nickel(II) complexes of phthalocyanines¹¹⁹ and the chelate β -ketoacetamidoimidazoquinoline complexes of a series of *d* elements,¹²⁰ which exhibit a very high resistance to the action of radiation and corrosive agents in the environment, be employed. In a series of studies carried out in recent years, the possibility of using the coordination compounds of nickel(II),^{121–125, 131, 133, 135} cobalt(III),¹²⁸ and also platinum group metal ions, in particular those of rhodium(III)¹²⁹ and palladium(II),^{123, 125, 131, 137} in the colour diffusion photographic process has been considered. Judging from all the available evidence, a very large number of coordination compounds with structurally cumbersome N,N'-N,O-, and N,S-chelating and especially macrocyclic ligands having high extinction coefficients in the visible part of the spectrum are suitable for effecting the colour photographic process with diffusional transfer of the image.^{129, 131} The use of compounds **38–40** is associated primarily with their availability and low cost.^{110, 138, 139}

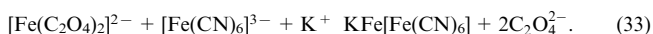
IV. Chelate and macrocyclic complexes as the 'active principle' of nonsilver photographic systems

Several decades before the silver halide photographic process saw the light of day, namely in 1831, Döbereiner already observed that potassium tris(oxalato) ferrate(III) $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$ exhibits an extremely high sensitivity to ultraviolet and blue radiation. Döbereiner's observation for a long time failed to attract the attention of investigators even despite the fact that in 1842 J Herschel created on its basis a fundamentally new, for the time, method of recording information — the so called cyanotype method. Its essential feature reduced to the fact that the photolytic redox process



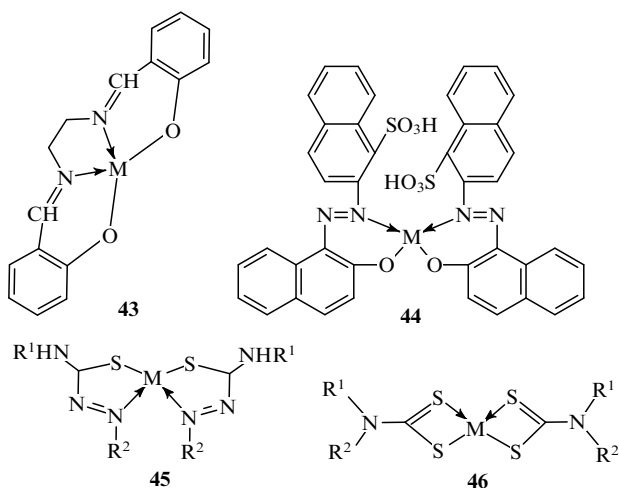
occurred on the sections of the paper impregnated with $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$ solution subjected to illumination by quanta in the ultraviolet and visible (blue zone) regions of electromagnetic radiation.

The 'working material' for the generation of the visible image was in this case the hexacyanoferrate $\text{KFe}[\text{Fe}(\text{CN})_6]$, which was formed on the exposed sections of the photomaterial, treated with an aqueous solution of potassium hexacyanoferrate, in accordance with the following reaction:

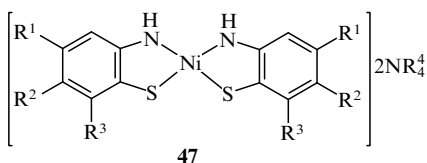


The unexposed sites remained unchanged after treatment of the exposed photomaterial with $\text{K}_3[\text{Fe}(\text{CN})_6]$ solution. This resulted in the formation of a blue image on a white background. This process was used in practice (mainly for copying work) up to the 1960s; nowadays it has been displaced by improved methods (in the first place xerox copying) and it is therefore of only historical interest. However, the problem of the search for systems which are not inferior to silver halides as regards their sensitivity to visible radiation remains of current interest.¹ In this connection, the attention of investigators has been attracted by the coordination compounds of *d* elements with chelating and macrocyclic ligands; one cannot rule out the possibility that in the future photographic materials based on them will prove capable of offering serious competition to AgHal light-sensitive systems.^{141–145}

Coordination compounds with N,O- and N,S-ligands, in particular with the azomethines **43** and azo-dyes **44**,^{146–150} 8-hydroxyquinoline, anthra-quinone and its derivatives,¹⁵¹ various substituted derivatives of dithione and dithiocarbamic acid (compounds **45** and **46**),^{152–154} and the structurally similar compound **47**¹⁵⁵ have been proposed as reagents suitable for recording UV and visible radiation.

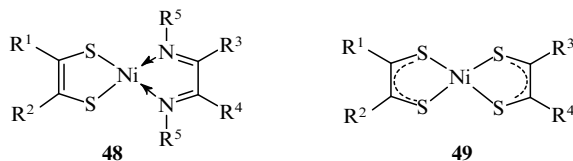


M = ion of 3d element; R¹, R² = Alk, Ar;

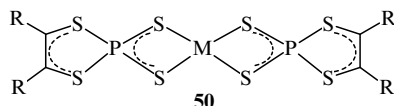


R¹, R², R³ = H, Alk, NO₂, Hal, NR'₂.

Also proposed have been a series of coordination compounds with dithiolate ligands (in particular complexes **48–50**),^{156–161} *i.e.*

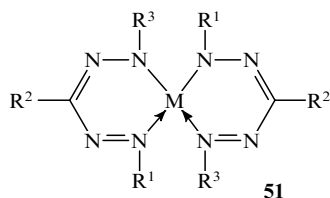


R¹–R⁵ = Alk, Ar;



M = V, Ni, Cu, Pt; R = Ph, Ar, AlkO

and with N,N-donor ligands,^{162–189} among which special mention should be made of the zinc(II), cobalt(II), and mercury(II) coordination compounds of benzindolinospiropyrans,¹⁶² the copper(II) complexes of 1,2-ethylenediamine and its analogues [CuL_n](BR₄)₂ (n = 2–4, R = Ar),^{163,164} and compound **51**.¹⁶⁹

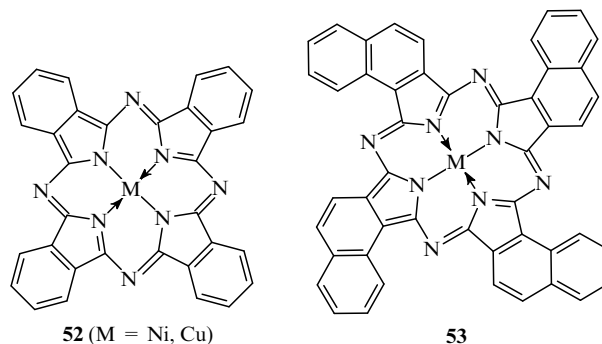


M = Mn, Co, Ni, Cu, Pd, Pt;

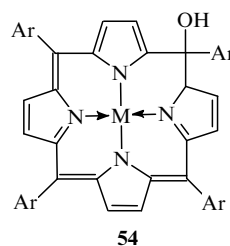
R¹–R³ = H, Hal, OH, COOH, Alk, AlkO, Ar.

However, coordination compounds with various phthalocyanine ligands, the simplest of which is complex **52**, aroused the greatest interest. Initially complexes of this type were used as carriers of the nonsilver photographic image;¹⁷⁰ however, the role of the light-sensitive compounds was assumed by coordination compounds of the type [PdL_mX_n]_kY_l [L = sterically hindered polydentate ligand of the type of 1,1,7,7-tetraethyldiethylenetriamine; X = Cl, Br, N₃, SCN; Y = Cl, Br, N₃, SCN, B(OR)₄; m, n = 1,2; k, l = 1–4] while the leuco-forms of the phthalocyanine

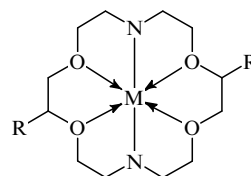
complexes served as a kind of 'developing substances'. However, studies have been published recently^{171–186} where macrocyclic coordination compounds of this kind were used this time as radiation receptors. Thus Mn(III) and V(IV)O alkylphthalocyanines have been proposed for the recording of information with the aid of a semiconductor laser,¹⁷¹ 1,2-benzophthalocyanines **53** have been proposed as optical recording materials,^{172,176} and fluoroalkylated phthalocyanines have been suggested for the recording of laser radiation.¹⁷⁷



The use of coordination compounds of 3d elements with related phthalocyanine ligands, in particular the cobalt(II), nickel(II), and copper(II) complexes of substituted tetrapyrizinoporphyryns^{187,188} and the gold(II) and palladium(II) complexes of hydroxyphlorins (complexes **54**)¹⁸⁹ as light-sensitive reagents has also been described.

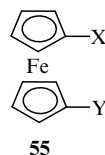


Quite a few instances of the successful employment of coordination compounds of metals with hydroxyacids (the photochromic properties of such compounds have been known for a long time) as well as other O,O-ligands (in particular β-diketones and crown-ethers^{190–200}) are known.



M = Co, Ni, Cu.

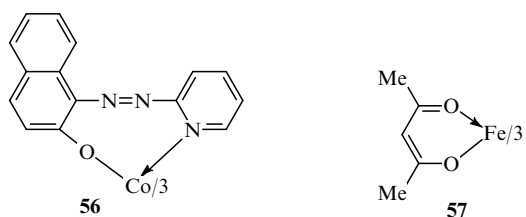
There are also literature data concerning the fairly high sensitivity of carbonyl and cyanide complexes to UV and visible light quanta,^{200–205} in particular their practical application as the active principle in a series of photochromic systems.^{206,207} The use of ferrocene and its derivatives,^{208–215} for example the products of its interaction with the salts of quaternary heterocyclic bases,²⁰⁸ for this purpose is extremely instructive. Thus photographic emulsions recording radiation as far as the blue-green region of the visible spectrum have been prepared on the basis of complex **55**.



X, Y = CO(CH=CH)_nAr (n = 1, 2)

In certain nonsilver systems based on the titanium(IV) chelate complex of 8-hydroxyquinoline,¹⁵² it was possible to achieve a comparatively high sensitivity of the photographic emulsions to light quanta over the entire visible range (400–700 nm), but the level of sensitivity of the AgHal photographic materials in the same range has not so far been attained. In most cases, the coordination compounds with chelate and macrocyclic ligands are sensitive only to radiation in the UV and blue-violet (< 430 nm) spectral regions furthermore, the lower limit of the level of radiation per unit surface of the photographic emulsion which they are still capable of detecting (it can be regarded as a kind of characteristic equivalent to photographic sensitivity) is $\sim 10^{-3}$ J cm², whereas for modern silver halide photographic systems it is close to 10^{-7} J cm².²¹⁴ Data concerning the possibility of using the coordination compounds of metals with chelate and macrocyclic ligands for the recording of streams of fast electrons, X-rays, γ -rays, and other types of high-energy radiation are more promising in this connection.^{216–229} In particular, the ferrocenyl complexes **55** as well as the analogous nickel(II) cobalt(II), chromium(III), and titanium(IV) complexes, already mentioned above, have been used for this purpose, as a result of which it proved possible to record electron streams and X-rays with energies up to 20 keV.

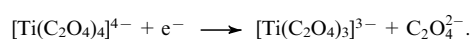
Even more interesting data have been obtained on cobalt(II) chelate complexes with 1-(2-pyridazo)-2-naphthol ligands (complex **56**), *i.e.*



which in terms of sensitivity to ionising radiation in general and to X-rays in particular are superior to silver halides. The copper analogue of complex **56** with a metal ion : ligand ratio of 1 : 2 also exhibits a fairly high sensitivity to electron streams.²²³ The coordination compounds of cobalt(III) with other tridentate ligands, in particular with 1-(2-pyridyl)-, 1-(2-thiazolyl)-, and 1-(2-oxazolyl)-formazans, and also with 1-(2-pyridyl)-1-(2-quinolyl)-dithiooxamide may also serve as the active principle in light-sensitive systems.²²⁰ A comparatively high sensitivity to X-rays has been noted also in the iron(III) chelate complex of acetylacetone **57**.²¹⁹

The same complex can be used for the reception and brief fixation of information under the influence of high-intensity radiation, in particular laser radiation. There is no doubt that the list of coordination compounds of *d* elements with chelating and macrocyclic ligands may increase appreciably in the future. Bearing in mind that silver halide photographic materials with extremely high AgHal concentrations per unit surface are used for the recording of hard ionising radiation in medical and especially industrial radiography,²³⁰ the interest of investigators in these materials becomes understandable.

Unfortunately at the present time there have been few detailed studies of the mechanisms of the formation of nonsilver images in light-sensitive systems comprising coordination compounds with chelating and macrocyclic ligands.^{175, 195, 231–233} The mechanism of the formation of images in photographic emulsions containing organopolysilanes and titanil(IV) phthalocyanine as a result of their exposure to UV radiation has been examined.¹⁷⁵ The photo-colouring process and the photodecolorisation of titanium(IV) coordination compounds of hydroxy-acids under the influence of UV and visible radiation has been investigated; the authors¹⁷⁵ believe that the photochromism observed in this case is associated with the redox process



This hypothesis is supported if only by the fact that the colour of the photochromic solution vanishes not only in the dark but also on oxidation, for example by atmospheric oxygen.¹⁷⁵

A short but extremely interesting paper²³² in which the mechanism of the absorption of radiation by the chromium(III), iron(III), cobalt(II), nickel(II), and copper(II) coordination compounds of azo-dyes, in particular 2-hydroxyphenylazo-2-naphthol and 2-carboxy-4-methylphenylazo-4,5-diphenyltriazole also merits attention. A relation has been established between the ability of these compounds to record radiation and the formation in their presence of singlet oxygen. The image formation process in photographic emulsions based on ferrocene has been examined^{212, 215} and the effect involving the reversal of the image under the influence of a small amount of reagents capable of forming stable coordination compounds with iron(II) and iron(III) was noted. In this connection, the hypothesis was put forward²¹² that such reagents bind iron(II) and (or) iron(III) and eliminate them from the autocatalytic process involving the reduction of ferrocene and actually play the role of a kind of inhibitors (the virtually complete inhibition of the development process is observed even at extremely low concentrations of these substances, namely ~ 0.003 M).

An attempt has been made to interpret the light-sensitive properties of tris(2,2-bipyridyl)ruthenium in photoinduced film stencils made from organic pigments,²³³ whilst in another study²³¹ photographic systems with an 'active principle' comprising copper(I) and cobalt(III) coordination compounds were considered; mechanisms of the formation images on the corresponding photographic materials have been proposed in individual instances.

Overall, it is essential to note that, despite the existence of a fairly considerable set of review articles and monographs (see, for example, Refs 138–145, 234, and 235), the studies on the mechanisms of the formation of photographic images on nonsilver light-sensitive materials are narrowly specific and scattered. Furthermore, the sensitisation possibilities remain completely undiscovered for nonsilver photographic systems based on coordination compounds of *d* elements with chelating and macrocyclic ligands (as is the case for AgHal photographic materials), so that the true potential possibilities of such light-sensitive systems remain in essence completely unknown. The sensitometric characteristics of the nonsilver photographic materials which might be realised in practice by varying the processes involved in their chemical-photographic treatment also still remain obscure. The mechanisms of the formation of catalytic centres in nonsilver light-sensitive systems based on coordination compounds with chelating and macrocyclic ligands have also been inadequately investigated. (In the vicinity of these centres, the development reaction, accompanied by the formation of a carrier of the nonsilver image in the photographic emulsion, is known to occur first of all.^{2, 3}) The coordination of the efforts of specialists in two extremely remote fields of science — the photochemistry of the information recording processes and coordination chemistry — is essential for the successful solution of the problem. Unfortunately one has to conclude that in recent years interest in the search for and study of nonsilver photographic systems based on chelate and macrocyclic coordination compounds has appreciably diminished despite the fact that there has been no real increment in the extraction of silver throughout the world and, judging from all the available evidence, cannot be expected in the foreseeable future.

V. Conclusion

The nonsilver photographic systems and photographic images examined in this review, the carriers of which are coordination compounds of *d* elements with chelating and macrocyclic ligands, are of considerable interest both for photographic science and for the chemistry of coordination compounds. The generation of metal chelate photographic images can increase in many instances the information content in light-sensitive materials. Furthermore,

one may expect in the future also the creation of a colour photographic process analogous to current silver halide colour photography, in which the image carriers will be coordination compounds of *d* elements with chelating and macrocyclic ligands. They will ensure the highest resistance of photographic materials to the action of light and corrosive agents in the environment. There are all possible grounds for the assumption that, as new experimental data accumulate, this global problem in modern photography will be successfully solved.

As regards the chemistry of coordination compounds, the synthesis of complexes of 3*d* elements with chelating and macrocyclic ligands marks the appearance of an independent scientific discipline — the study of the reactivities of polymer-immobilised coordination compounds with fixation of the substance by intermolecular forces and the discovery of the rules governing complex formation involving such compounds.⁹

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Polymer-immobilised nanoscale and cluster metal particles

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Abstract. The essential data on the immobilisation of nanoscale and cluster metal particles in polymeric matrices are considered and systematised for both macroligands and the matrices formed *in situ*. Special attention is paid to the controlled chemical passivation (stabilisation) of extremely active particles of colloidal size using high-molecular-weight compounds. The routes of formation of polymer-immobilised nanoparticles directly in the polymer medium are analysed. This allows the preparation of compositions characterised not only by the most regular distribution of these particles over the bulk of polymer but also by a strong chemical interaction between the components. Studies in the field of polymer-analogous transformations, which offer a promising approach to the binding of mono- and heterometallic clusters as a new direction in the physicochemistry of nanoparticles, are discussed in detail. The peculiarities of the immobilisation of clusters, polynuclear structures, and nanoparticles by synthetic polymers, on the one hand, and by biopolymers, on the other hand, are considered. The basic fields of the application of the products obtained and the prospects of the development of this direction are outlined. The bibliography includes 394 references.

I. Introduction

The possibility of combining the physicochemical properties of metals and polymers in a single material and of regulating these properties through concentrational changes has long been under discussion.^{1,2} The progress in this direction is stimulated by the ever-growing interest in this problem shown in many fields of chemistry, physics, and materials science. Numerous materials have been already produced, that are unique with regard to their mechanical, electrophysical, magnetic, optical, catalytic, and often biological properties. Two major stages may be differentiated in the development of this direction. At the beginning, major attention has been given to the development of convenient and reproducible techniques for the synthesis of ultrasmall metal

particles of nanometre size (with parameters not exceeding 100 nm in at least one dimension), their improvement, and bringing into practical usage. The second stage of studies in this field focused on the development of effective methods for the stabilisation of metal nanoparticles with the help of polymers.

These studies were largely advanced by the development of metal–polymer (metal-filled) composite materials (nearly single-phase, sufficiently homogeneous, and relatively stable systems) possessing specific physicochemical and mechanical properties: increased heat and electric conductivity, high magnetic susceptibility, and the ability to shield from ionising radiation. Specifically, these materials meet the major requirement for protective screens by providing the predetermined degree of decrease in radiation at minimum weight. Metal-polymer composite materials are most widely used in the electronics and radio engineering for producing electroconductive pastes and glues (in particular, printed circuit boards), special coatings (paint and varnish), photo- and X-ray-resistors, X-ray-contrast polymers, rheomagnetic fluids, as well as in instrument building, aviation, and space technology. The spectrum of practical uses of these materials has been much expanded by the discovery of their specific catalytic properties,³ which display close similarity to those of polymer-immobilised catalysts,^{4–5} by their application in chemisorptional and photographic processes (including the production of magnetic developers for xerography and photorecording media) and in the synthesis of antifrictional polymeric coatings, *etc.* Investigation of the interactions in the macroligand–nanoparticle systems may provide additional information on both the principal structural elements of the latter and the peculiarities of the surface of polymers. Finally, it is well known that the nanoparticles of certain metals are endowed with biological activity: they are used as effective drugs in medicine and plant protectors in agriculture.⁶ Many polynuclear enzymes are known to contain clusters of metals (*i.e.*, essentially ultrafinely dispersed particles) bound to biopolymers.^{7,8} Thus, there are certain common characters in the behaviour of metal nanoparticles in synthetic polymers, polymer-immobilised clusters, and metal clusters (polynuclear structures) in biopolymers.

To date, especially over the last 10–15 years, a large body of diverse information has been accumulated on basic techniques for the preparation and investigation of the structure and properties of polymer-immobilised nanoparticles; nonetheless, all these data stand in need of adequate systematisation. Some of the relevant

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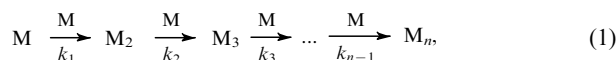
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problems have been considered recently in the example of nanoparticles and clusters of the platinum group metals in polymers.⁹

II. General characterisation, methods of preparation and some properties of the metal nanoparticles

Small n -nuclear particles, which are structural elements of ultra-finely dispersed powders, occupy the intermediate position between clusters and massive metals. On transition from a single atom in the zero valence state (M) to a metal particle endowed with all of the compact metal properties, the system passes through a number of intermediate stages,



among which the principal is the formation of clusters and nanoparticles characterised by small sizes of their morphological elements. This is followed by the formation of large stable particles of a new phase. The process of collectivisation of electrons in the core that is formed occurs spontaneously and is in essence similar to the formation of molecules from individual atoms. The attribute 'metallic' reflects solely the composition rather than the nature of these particles, which are regarded as transient species between the bulk metal and its individual atoms. Clusters are figuratively called metal embryos.¹⁰ The extent of dispersion has a crucial influence on their chemical activity, and as a metal particle grows larger its properties change substantially. With regard to their size, such particles may be divided into three following types:¹¹ nanometric (ultradispersed) (from 1 to 30–50 nm),¹² highly dispersed (from 30–50 to 100–500 nm), and micrometric (from 100–500 to 1000 nm). The latter are as a rule composed of individual particles and their aggregates, being mono- and polycrystals of the fractal type. The particles of the first two types are called colloidal, while those of the third type are known as coarse-dispersion particles. When prepared under normal conditions, the aerosol metal particles with a mean size of ~50 nm have the spherical or a close to spherical shape owing to their high surface energy.¹³

The terms 'ultrasmall particles', 'nanocrystals' (for designating the metal nanoparticles whose size ranges from 2–5 to 50 nm),^{14, 15} and 'colloidal crystallites'⁶ are also frequently used. The requirements for the size of nanocrystals of semiconductors in polymeric matrices boil down to the following:¹⁷ the upper limit of their size should allow the optical homogeneity of a composite material (light is not scattered by the media composed of particles with the size below 1/4 of the light wavelength), whereas the lower limit is determined by the very fact of the existence of crystalline particles (the boundary of transition from the crystalline to the quasi-molecular phase). The notions of 'molecular aggregation' and 'crystalline clusters' are used less frequently.¹⁸

Naturally, a process occurring according to the Eqn (1) is not reduced to a trivial mechanical build-up of metal atoms involved in the formation of n -nuclear constructions. It is common practice to differentiate two types of nanoparticles: clusters, *i.e.*, the particles with ordered structures (their size ranging from 1 to 10 nm) composed as a rule of 38–40 (sometimes more) metal atoms, and the nanoparticles proper (disordered structures), having a size of 10–50 nm and including in most cases 10^5 – 10^6 atoms.

It is known that the cluster formations are characterised by a non-monotonic dependence of their properties (*e.g.*, ionisation potential and bond energy per metal atom, interatomic distances, optical and magnetic properties, electron conductivity, electron–substrate interactions, *etc.*) on the cluster size, *i.e.*, on the number of metal atoms incorporated. It is these criteria that determine the existence of the so-called 'magic numbers': a discrete set of numbers of atoms (N) corresponding to the formation of the energetically most favourable clusters.¹⁹ These

numbers equal to 13, 55, 147, 309, 561, 923 ... are calculated by the formula²⁰

$$N = \frac{1}{3}(10n^3 + 15n^2 + 11n + 3).$$

The structure of small and medium-size homometallic clusters (3, 4, 5, 6, 10, 20, and 38 atoms) has been established by X-ray diffraction analysis.²¹ Their metallic framework consists mainly of cycles, carcasses, and polyhedra. On going from clusters to nanoparticles, the non-monotonic character of structures becomes less pronounced. Still, the symmetry in the distribution of acting forces is violated because of the non-compensated character of bonds at atoms localised in the subsurface layers, *i.e.*, having neighbours mostly on one side (they amount a substantial proportion of the total number of atoms in a particle). As regards their properties, these 'ligand-deficient' atoms are to a certain extent similar to the superficial atoms of crystals. The disposition of atoms at the interface, their interaction with neighbours and motions near the crystal facets predetermine disturbance in the translational symmetry, strong anisotropy, a pronounced anharmonic character of oscillations, *etc.*^{10, 13, 22–25} This results in the enhanced adsorption potential of such atoms, larger possibilities of ion and atom exchange, contact interactions of structural elements, *etc.* However, there appear difficulties in the interpretation of their behaviour due to the impossibility of distinguishing between the bulk and surface properties of these particles. Furthermore, if the parameters of their structural elements are commensurate at least in one direction with the correlation radius of a definite chemical or physical phenomenon (*e.g.*, with the length of free path of electrons, phonons, the coherence length in a superconductor, the size of a magnetic domain or a nucleus of a new phase, *etc.*) or are less than this radius, such systems or the reactions involving them manifest the so-called dimensional effects.

Thus, the nanoparticles with highly developed interfacial surfaces possess excess energy in comparison with homogeneous materials, and they are often called energy-saturated systems. Their investigation is the subject of a new rapidly expanding branch of science, physicochemistry of nanoparticles (also known as nanotechnology and physics of clusters). Since the progress in this field is closely associated with the development of methods for the synthesis of nanoparticles, we shall briefly dwell on the main of them.

The spectrum of techniques used for the preparation of nanoparticles is rather broad and is based on two major approaches: physical and chemical. The former is largely based on condensation techniques consisting in the 'assembly' of nanoparticles from individual atoms of metals. By way of their gradual association and on reaching a definite size with the appearance of a clear-cut physical interface, these atomic aggregates become nuclei (embryos) of a new phase. The condensation methods include direct evaporation of metals, in particular with the use of Knudsen cells, induction heating, low-temperature condensation technology, spray and electron bombardment, condensation in electric arc discharges and by plasma techniques, explosion of conductors, *etc.* In most cases, these techniques prove to be mutually complementary rather than competitive. Less widespread are the techniques for preparing nanoparticles by dispersion of coarse particles (colloidal mills, shakers, sonication, high-frequency, and electric arc fragmentation, *etc.*).

Of the chemical methods, the most popular is the reduction of metals in solutions in the presence of different stabilisers dating back to the 19th century. Metal aluminium hydrides, borohydrides, amino boranes, hydrazine and its derivatives, hypophosphites, formalin, salts of oxalic and tartaric acids, hydroquinone, dextrin, a number of other compounds (H_2O_2 , H_2S , CO , CS_2 , NO , $SnCl_2$), and most often hydrogen serve as the reducing agents. The chemical methods also include diverse pyrolysis techniques of moderately stable metal compounds (carbonyls, formates, oxalates, organometallic compounds), various modifications of cryochemical synthesis, and plasmochemical techniques. As a rule,

the common disadvantage of chemical methods is the formation of polydisperse colloids with a wide particle size distribution.

A new direction in the physicochemistry of nanoparticles known as chemistry of 'giant' clusters deserves special mention. The most recent years witnessed the development of techniques for the synthesis of compounds with metal–metal bonds whose nuclearity may be as high as a few hundred units,[†] *e.g.*, Pd₅₆₁Phen₆₀(OAc)₁₈₀ or Pd₅₆₁Phen₆₀(PF₆)₆₀O₆₀,^{26,27} and even the compounds containing up to 1415 Pd atoms.¹⁰ In fact, these huge clusters are nanoparticles coated with a ligand envelope protecting them from environmental impacts.

The extremal conditions of the synthesis and a large specific surface of the nanoparticles characterised by a small size of morphological elements may induce changes in their physicochemical properties and even lead to the distortion of their atomic structure.²² Very high (or very low) temperatures, high rates of processes, various external impacts (*e.g.*, rapid condensation, annealing) favour the formation of non-equilibrium 'frozen' states in the growing *n*-nuclear particles.

A highly developed interface surface, excessive energy of superfacial atoms, and decreased activation energies of different reactions determine the extremely high reactivity of nanoparticles. Therefore, the energy-saturated nanoparticles produced under strongly non-equilibrium conditions are highly reactive towards the components of the medium they are formed in.[‡] When placed into an inert atmosphere, they usually undergo spontaneous aggregation leading to the eventual formation of powders with normal dispersity. In some instances, the exceptionally high chemical reactivity of nanoparticles is useful, though more frequently it poses a number of problems related to the necessity of their stabilisation for transportation and storage purposes. In this context, the search for effective ways of the controlled chemical passivation of nanoparticles is a topical problem. The solution of this problem is largely facilitated by a high adsorption capacity of these particles towards high-molecular-weight compounds.

III. Basic principles and mechanisms of the stabilisation of nanoscale metal particles by polymers

The interaction between nanoparticles and adsorbed macromolecules is the most important field in the modern science of polymeric colloids studying the regularities of the formation of the dispersion systems with highly developed interfacial surface, their kinetic and aggregative stability, diverse surface phenomena at the interface, and the adsorption of macromolecules on solid surfaces from liquid media.²⁸ The adhesion between polymers and metals is determined by a number of factors, among which the most essential are the nature of the molecular forces, surface defects, internal strain, and electrical charges. These factors influence the mechanism underlying the polymer–metal interaction.^{28–30} They are best described within the framework of the theory of 'molecular solder' (the term used for strong adhesive interactions between components),³¹ based on the concept of structural–mechanical factors of the stability of dispersion systems and spatial networks of the coagulation structure type.

[†] Strictly speaking, such huge clusters are not individual compounds but rather include particles of different size and composition within a narrow distribution range (similar to the molecular mass distribution of polymers). The idealised formulae used to describe them are averaged over a statistical ensemble.

[‡] The free energy variation during the dispersion of a homogeneous metal of volume *V* to particles with radius *r* is equal to

$$\Delta F(r) = \frac{\sigma V}{r},$$

where σ is the increment of free energy of a system during formation of a unit of new interfacial surface.

A colloidal system is formally composed of a continuous phase, dispersive medium (polymer), containing distributed nanoparticles representing the dispersed phase. A colloidal system is regarded as stable, when the dispersed phase exists in the form of individual isolated particles for a sufficiently long period of time (a few months or even years).[§] Sometimes, the sedimentation resistance is estimated from the quantity of pellet formed by centrifugation (*e.g.*, after a 20-min centrifugation of a Pt–polyvinyl acetate (PVA) system at 6000 *g*). The size of colloidal particles in the system Pt–PVA may be controlled by varying *g* and the centrifugation time.³⁷

There are two types of polymer-stabilised colloids: lyophobic and lyophilic. In the former, the interaction between the dispersive medium and the dispersed phase is so weak that such colloids prove to be unstable (in the thermodynamic sense) and the attractive forces lead to the aggregation of particles. Nonetheless, the existence of a noticeable repulsive barrier and the remoteness of particles from each other can slow down this process so that the system remains virtually unlimitedly stable (the kinetic stability). Sometimes, these colloids are called thermodynamically metastable. A typical way of achieving the kinetic stability of lyophobic particles is electrostatic stabilisation. On the contrary, the lyophilic systems are thermodynamically stable, *i.e.*, their total free energy of mixing is negative, and the dispersed state may be characterised as a low-energy state. The prime cause of the aggregational resistance of such particles is their solvation.

The aggregation of such systems is called coagulation, when densely packed aggregates are formed, or flocculation, when the particles remain separated from each other by a polymer. The coagulation of nanoparticles on polymeric surfaces is sometimes called heteroadagulation. The non-charged particles coagulate rapidly owing to the dispersional attraction (the London forces). This process is described by the rate constants of fast coagulation according to Smoluchowski: $k_c = 4kT/\eta$, where *k* is the Boltzmann constant, *T* is temperature, and η is the dispersive medium viscosity. The constant k_c characterises the long-range attraction between colloidal particles. The van der Waals attraction between individual atoms or molecules extends only over the distance of a few decimal fractions of a nanometre. However, in the systems under discussion, a polynuclear (multicentre) interaction takes place: each atom or molecule of an individual nanoparticle attracts each atom of another particle containing 10^6 – 10^{10} atoms. The interaction force of the particles in the dispersed phase in coagulation structures is estimated, on the average, as 10^{-10} N per one contact. Summation of a huge number of all possible interatomic interactions between nanoparticles results in a considerable attraction.

The potential attraction energy U_r between two spherical particles with radius *r* at the minimal distance between their surfaces l_0 may be described by the following simplified equation:

$$U_r \approx \frac{Ar}{12l_0} \text{ at } r \gg l_0,$$

where *A* is the effective Hamaker constant having the energy dimensions. In its order of magnitude, the constant *A* is close to *kT* for latex particles, though in the case of metal dispersions it may also have higher values. For example, for poly(methyl methacrylate) (PMMA), polystyrene (PS), Ag, and Al₂O₃, the values of $10^{20} A$ are 6.3, 6.15, 40.0, and 15.5 J, respectively.³⁸ Note for comparison that the attraction energy of two latex particles, each being 120 nm in size, is $\sim 10 kT$ at the distance of 1 nm and $2 kT$ at 5 nm. In the absence of repulsion between particles, this would be quite sufficient for coagulation, since by its absolute value, the energy of attraction is greater than the thermal energy of particles, equal to $\sim \frac{3}{2} kT$ for the three translational degrees of freedom.

[§] The theory of stabilisation of colloidal particles by polymers is considered in sufficient detail in Refs 32–36. We discuss here only the problems that are directly relevant to polymer-immobilised nanoparticles.

Hence, it may be assumed that in the systems under consideration the region of van der Waals attraction extends to the distance of 5 nm. The magnitude of London attraction and its action radius are the crucial factors in the choice of ways for the stabilisation of such particles.³² A long action radius of attractive forces restricts considerably the possibilities of stabilisation. It follows that the stability condition of nanoparticles requires the occurrence of repulsion between particles at the distances at least commensurate with the action radius of attraction. Coagulation takes place at isoelectric points (when the particle charge becomes zero).

In order to stabilise the 'ligand-free' clusters, use is made of matrices of inert gases, low temperatures, and surfactants. The hydrophobic nanoparticles are homogeneously dispersed inside the core of micelles at surfactant concentrations above the critical micelle concentration (CMC). At lower concentrations, the stabilisation is achieved by adsorption of surfactants on the surface of nanoparticles.

The most important are the electrostatic and polymeric methods of stabilisation (also known as charge and steric stabilisation). The latter is brought about by the adsorptional coating of the nanoparticle surface with macromolecules.

It is known that the size of gold nanoparticles is increased in the presence of poly-4-vinylpyridine (P4-VPy) that is indicative of the chemisorption of macrocations on them and the formation of a 'soluble complex'.³⁹ The mean hydrodynamic radius of such stabilised particles (21 ± 0.5 nm) is larger than that of nanoparticles in water (13 ± 0.5 nm) (Fig. 1). According to Kiwi and Gratzel,³⁷ the mean hydrodynamic radius of Pt particles stabilised with PVA with a molecular mass of 60 kDa is 10.5 nm, the size of metal particles being small compared with the thickness of the protective environment.

The possibility of polymeric stabilisation is determined by the condition that the spatial dimensions of even relatively low-molecular-weight compounds are comparable with, or larger than, the action range of the forces of London attraction of particles. Assuming the 'diameter' of a linear polymeric macromolecule to coincide with the root mean-square distance between its ends, the ratio of the particle radius to the molecular weight of a polymer (M_r) may be calculated by the expression³²

$$\langle r^2 \rangle^{0.5} \approx 0.06 M_r^{0.5}.$$

For the polymers with $M_r = 10^4$, $\langle r^2 \rangle^{0.5} = 6$ nm, whereas for $M_r = 10^5$, $\langle r^2 \rangle^{0.5} = 20$ nm.

Thus, the polymeric molecules with $M_r > 10^4$ have precisely the size range required for the stabilisation of colloidal particles (clearly, it is also necessary that the macromolecules induce repulsion of particles). Another necessary condition of the stabilisation is the ability of polymer to wet the nanoparticle surface,

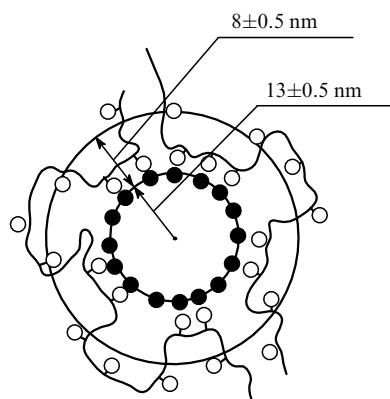


Figure 1. Structure of the 'soluble polyelectrolyte complex' formed by a gold particle and a polycation macromolecule.³⁹

and this in turn is dependent on the character of the interaction of the polymeric medium with the active centres of the surface.

The steric stabilisation of particles can follow two different mechanisms. The first mechanism assumes the attachment of macromolecules to the surface of particles, for example, by grafting or physical adsorption. In this situation, irrespective of the form of the molecules (unfolded or globular) localised on the surface of nanoparticles, their interaction is determined by the number of polar groups in the adsorbed polymer per unit surface. According to the second mechanism, stabilisation is performed by macromolecules from solution. A combined method of electrosteric stabilisation based on the use of the superficial charges on the particle or on the polymer, *e.g.*, on a polyelectrolyte, is frequently used (especially in biopolymeric systems, see Section VI).

The mechanisms of the stabilisation have not been totally clarified yet because of their complexity. Simultaneous occurrence and mutual influence of processes of particle enlargement and adsorption of macromolecules on the surface of both initial and formed particles is to be noted. Here, the aggregative stability depends on the ratio of coagulation and adsorption rate constants. By analogy with the sorption processes, the quantity of sol coagulated per unit surface within a definite time interval is calculated by the equation⁴⁰

$$q = \frac{(c_0 - c_e)V_1S_1}{m_2S_2},$$

where c_0 and c_e are the initial and equilibrium weight concentrations of a metal sol, respectively; V_1 is its volume; m_2 is the weight of the polymer; S_1 and S_2 are the specific surfaces of metal sol and polymer, respectively. In most cases, the 'sorption equilibrium' is reached within a few hours, while the calculated sorption isotherms have an S-like shape and are approximated by the Langmuir equation in its linearised form in the region of low concentrations of nanoparticles. This implies that the superficial layers of metal particles are formed on polymers following the pattern of molecular sorption.

Simulation of the adsorption-coagulation processes is a rather difficult task. Let us confine ourselves to a mere listing of the most significant effects.³² The case with attached macromolecules involves elastic homosteric and enhanced steric stabilisation, flocculation (phase partitions, substitutive coagulation, crystallisational coagulation), and heterosteric stabilisation (selective flocculation, heteroflocculation, phase separation). In the case of free macromolecules, there occur substitutive stabilisation, flocculation, and phase separation. The efficiency of the sorption processes, to which the coagulation of nanoparticles is also referred, is determined by the overall balance of surface forces in the course of interaction of phases of different nature.⁴¹ Thus, the stabilising effect of polymers, often called shielding with a protective colloid,⁴² is the consequence of the adsorption of macromolecules on the surface of nanoparticles. By enveloping the nanoparticles, the macromolecules make them less sensitive to the action of electrolytes.

The attempts aimed at the quantitative estimation of the stabilising capacity of polymers date back to the times of Faraday (1857) who studied the effect of gelatin on the variation of the gold sol colour from red to blue upon addition of NaCl.

This phenomenon called subsequently protective action is associated with the ability of soluble polymers to prevent the coagulation of sol by electrolytes. To characterise various biopolymeric stabilisers, the notion of 'golden number' was introduced as the quantity of polymer (mg) capable of averting the flocculation of 10 ml of gold sol upon addition of 1 ml of 10% NaCl solution. The lower is the 'golden number' the more effective is the polymer in preventing the coagulation of the dispersed phase. Despite a sceptical attitude of some investigators¹ to such empirically established 'numbers', we believe that they are definitively useful for comparative analysis. For example, the 'golden numbers' for gelatin, albumin, gum arabic, and dextrin are 0.005–0.01, 0.1–0.2, 0.15–0.25, and 6–20, respectively.

The protective capacity of a polymer, *i.e.* its ability to stabilise colloids, is sometimes estimated as the weight of gold (g), which is stabilised by 1 g of polymer added to 1% aqueous solution of NaCl.⁴³ The protective capacities of gelatin, polyvinylpyrrolidone (PVP) with the mean degree of polymerisation $P = 3250$, polyvinyl alcohol (PVAI, $P = 500$), polyacrylic acid (PAA), and polyethylenimine (PEI) are 90, 50, 0.07, and 0.04, respectively. The ability of polymers to stabilise dispersions increases as their protective capacity increases. The critical concentration of KCl ($10^3 c_{\text{KCl}}$) required for the change of the colour of gold sol from red to blue in the presence of a definite concentration of polymer (1.0 g litre⁻¹) is also used for the evaluation of the stabilising capacity of polymers. It is significant that c_{KCl} is also sensitive to the molecular mass of polymers. For example, the value of $10^3 c_{\text{KCl}}$ varies from 12.5 (in the absence of polymers) to 18, 22, 47, and 480 in the presence of polyethylene oxides with molecular masses of 600, 4000, 6000, and 9000 Da, respectively.

A number of classical studies have established the physico-chemical base of the existence of gold sols, their morphology, and structure.[¶]

The strength and rigidity of protective layers, their spatial extent, as well as the mode of polymer adhesion to the particles are the most important characteristics of the stabilising effect. Polyelectrolytes or relatively rigid non-ionic macromolecules may be attached by adsorption either by their one end ('tails') or both ends ('loops'). The adsorption in the form of loops is most characteristic of homopolymers. As a rule, homopolymers are rarely used as steric stabilisers because they are driven out of the interaction zone in the process of Brownian collisions of particles. However, their efficiency is substantially enhanced when there are centres of specific interaction in the homopolymers themselves or on the surface of the particles to be stabilised. Most often this concerns the protective action of polynucleotides possessing in their native state a complex architecture (secondary, tertiary, and even quaternary). Therefore, they bring about simultaneously both electrostatic and polymeric stabilisation.⁴⁵

Here, the polymeric chain itself may undergo various conformational transformations. In this connection, it seems appropriate to mention the problem of 'blue silver': the radiation-chemical reduction of Ag^+ ions in slightly alkaline aqueous solutions is accompanied by the appearance of bright-blue colouration in the presence of PAA.^{46,47} The reduced 'blue silver' possesses high stability even when exposed to air and may be isolated in the pure form by evaporation of water. This phenomenon is due to the stabilisation of silver by PAA. In alkaline solution, the PAA molecules become unfolded owing to the repulsion of groups COO^- , providing Ag^+ ions with the possibility to interact with groups COO^- . Further Ag^+ reduction leads to cluster formation.

Another example is the stabilisation of $\text{Fe}(\text{OH})_3$ particles containing up to 120 iron atoms[†] in the presence of PVAI or polyvinyl esters with different degrees of polymerisation (Fig. 2).

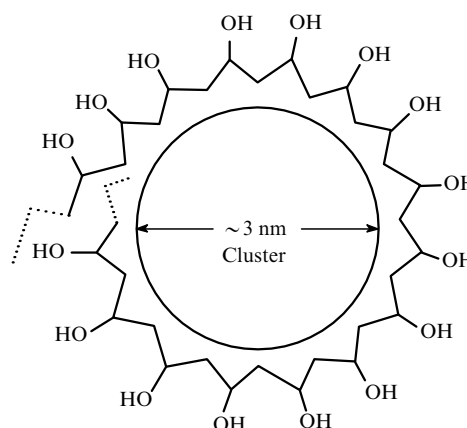


Figure 2. The 'inclusion' complexes consisting of PVAI and $\text{Fe}(\text{OH})_3$ -like clusters with hydrophobic bonding.

The optimum synthetic stabilisers are amphiphilic polymers, block- or graft-copolymers, which have one fragment ('anchor') in the form of a polymer insoluble in the dispersive medium, whereas the second part of the macromolecule is, on the contrary, soluble in this medium. A characteristic example may be polystyrene-block-polybutadiene subjected to epoxidation with subsequent modification by different nucleophiles.⁴⁸ The micelles of these copolymers in toluene dissolve salts of noble metals, as well as Zn and Cu, which are insoluble in pure toluene. The polymer-stabilised particles formed have the size of ~ 10 nm and are characterised by low polydispersity. Statistical copolymers are less effective.

As a rule, the anchor fragments are attached to the particles as a result of either physical adsorption (which is interpreted in a simplified approach as including processes determined by the van der Waals forces, dipolar interaction, or weak hydrogen bonding which is easy to break), or chemisorption (caused by strong specific bonding of the electrostatic or covalent nature, or by the acid-base interaction). The stabilising fragments ensure the steric protection owing to their mutual repulsion. This occurs in the following manner. When particles come close to each other in the course of the Brownian motion, the fragments are subjected to a stress generated by the compression of adsorption polymeric layers (in the collision of particles, the mutual penetration of polymeric chains is either weak or absent). The release of macromolecules from the region of strong compression requires either their desorption or displacement over the surface out of the stress zone, which demand a significant energy expenditure.

Naturally, in real systems the extreme adsorption of polymeric chains is often not achieved and there are superficial sites unsaturated with macromolecules. In addition, when the compression stress is sufficient for the desorption of macromolecules, the displacement of chains leads to their concentration at particular sites of the overall surface, and this process is accompanied by a decrease in the surface entropy. Furthermore, it is necessary to take into account the presence of defects in any metal surface, in particular, an almost unavoidable existence of an oxide film whose properties strongly depend on the nature of the metal. This leads to an enhanced adhesion due both to formation of hydrogen bonds between certain units of the macrochain and the oxide film and to 'infiltration' of polymers into surface defects or into a relatively porous oxide layer. Moreover, if a polymer contains hydroxyl, carbonyl, and other functional groups, there appears a possibility of heterogeneous chemical interactions. Preliminary treatment (lyophilisation) of the surface of nanoparticles or polymers with specific reagents may lead to the appearance of sites with increased electron densities. They play the role of preferential centres for the formation of nanoparticle primers

¶ There are two basic approaches to the preparation of stable monodisperse sols of colloidal gold:⁴² (a) disintegration of metallic Au by an electrical arc in a liquid medium and (b) reduction of gold halides (most often, HAuCl_4) by sodium citrate at 100 °C or by sonication under conditions of pulse or laser radiolysis. In a standard citrate sol, the gold particles are charged negatively, which is due to strong adsorption of citrate ions the charge of which is equilibrated by weakly bound sodium ions. The charge of gold particles may be positive, if the citrate is removed by filtration through an ion-exchange column with subsequent treatment of solution with *N*-hexylpyridinium polyethylene bromide. The positively charged polymer is strongly adsorbed on gold (the size of sol particles is 10–20 nm), while the bromide acts as the counterion.

† Hydrolysis of Fe^{3+} in aqueous solutions leads to the precipitation of particles $\text{Fe}_x(\text{OH})_{3-x} \cdot n\text{H}_2\text{O}$ in which the values of x and n depend on the reaction conditions; in some cases $\alpha\text{-FeO}(\text{OH})$ with a mean particle size of 2 nm is formed instead of $\text{Fe}(\text{OH})_3$.³⁵

(embryos). For example, treatment of gelatin with bromine facilitates its subsequent decoration with gold.⁴⁹

One should also take into account that ionomers manifest a clear-cut trend toward the association of ionic groups, which form ionic regions as a separate microphase in hydrophobic polymers. For instance, perfluoroalkylsulfonic acid (trade name 'Nafion') revealed morphological formations with ionic regions 3–4 nm in diameter generated by the sulfonate groups. These domains are connected by hydrophilic channels about 1 nm in diameter surrounded by fluorocarbon matrix (Fig. 3). These areas become the sites of concentration of ionic centres for the preferential formation of metaloclusters.⁵¹ In matrices of this type, a restricted diffusion of nanoparticles is observed. In pores of solvated polymeric networks, the coefficient of restricted diffusion of iron hydroxide particles (3–9 nm) exceeds $2 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$.⁵²

In conclusion of the brief discussion of the modes of stabilisa-

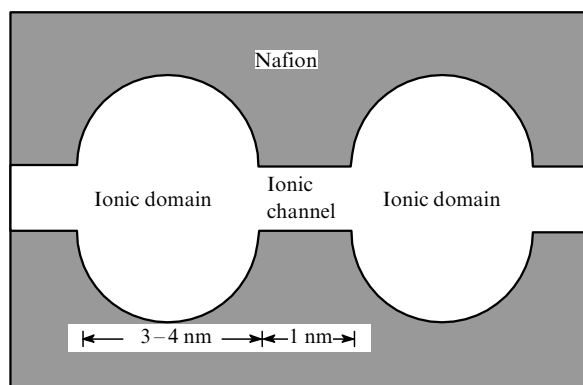


Figure 3. Schematic diagram of ionic domains in the Nafion ion-exchange resin.

tion of nanoparticles, let us dwell on the following points.

Although the basic theoretical concepts of the formation and stabilisation of colloidal dispersions refer primarily to polymeric emulsions (latex polymerisation of vinylic and diene monomers, the directed choice of emulsion paints and surface coatings, *etc.*), they also seem to be well applicable to the problem of nanoparticle stabilisation. The differences would most likely be of a quantitative rather than qualitative character. Specifically, as noted above, the attractive forces between particles of dispersed organic polymers are considerably weaker than between particles of metals, their oxides, and salts (cf. the above-mentioned values of Hamaker constants).

The quantitative theory of stabilisation of colloidal particles is based on the analysis of dilute colloids, one of their principal properties being the kinetic (sedimentation) stability. In the case of concentrated, and particularly highly concentrated (containing up to 80% of metal powder) systems, the involvement of the dispersed phase particles in the Brownian motion does not play any critical role. According to the expert view of P A Rebinder, their distinctive features such as strongly developed interfacial surface and high concentration of the dispersed phase in a liquid dispersive medium result in a major consequence: within the concentrated systems, thermodynamically stable spatial structures appear spontaneously as a result of mutual cohesion of particles inside the dispersed phase.³¹ The participation in the Brownian motion of nanoparticles, which are fixed in a spatial network owing to the atomic or coagulative contacts between the particles, is limited to oscillations around the equilibrium position. Indeed, the energy of thermal motion ($3/2 kT$) is much lower than the total energy of the interaction of neighbouring particles, which is determined by the nature of the elementary contacts, their number, and the distribution pattern in structures. Therefore, the

protective high-molecular-weight compounds and dry compositions of dispersed phases of sols are used in the preparation of concentrated hydrosols.

The protected sols acquire the properties of reversible colloids: the dry dispersed phase remaining after the evaporation of the dispersive medium can reform a stable sol upon repeated contact with this medium. In these systems, the lyophobic nanoparticles appear to be in a cobweb of the protective polymer. Such materials find diverse applications, because the practically valuable changes in their properties (higher thermal and electrical conductivity, heat capacity, ability to screen radiation, *etc.*) are realised only at large concentrations of nanoparticles (most frequently, above 50 vol.%, or 90 mass %). However, high viscosity of the molten polymeric matrix does not allow one to achieve regular distribution of nanoparticles, and this degrades the dielectric and mechanical parameters of the materials produced. Thus, the distribution character of nanoparticles in polymers is also significant from the practical viewpoint. For numerous purposes, it is important to achieve the formation of fractal clusters (fractal aggregates) *via* definite physical processes of growth in polymeric media.[‡] The fractal cluster is close to the percolational one⁵⁴ that makes it possible to realise transfer processes (in particular, the system conductance).

The above-discussed concepts refer to the bulk stabilisation (in solutions, gels, swollen polymers). Though, stabilisation often takes place on the surface (*e.g.*, in thin films or a thin subsurface layer of a polymer powder). Furthermore, natural 'cavities' are nearly always present in real polymers with a high degree of crystallinity, *e.g.* in polyethylene (PE) or polytetrafluoroethylene (PTFE) in which this index is 60%–85% and 75%–80%, respectively. Their existence is due to the peculiarities of polymeric chain packing upon transition from the amorphous to the crystalline phase. The amorphous regions are looser and include considerably more cavities, since here the cross-linking of macrochains is weaker than in the crystalline blocks. In these cavities, nanoparticles may be localised and stabilised. For example, the 'ligand-free' iron clusters (up to 35 mass %) are stabilised in the PE or PTFE matrices with a fairly narrow range of their sizes (the distribution maxima were observed for the particles measuring 1.48 and 1.81 nm, respectively).

A crucial role is also played by the pore size, which is one of the basic factors determining the stabilising capacity of matrices. The pores act as transport arteries for the penetration of nanoparticles or their precursors into the bulk of polymers. The incorporation of nanoparticles can also distort considerably the polymeric structure itself. The porosity is estimated from the specific surface (S_s), total volume (V_0), and radius (r) of pores and depends on many parameters, the most essential being the cross-linking density. With regard to their size, all pores are arbitrarily divided into three groups: micropores ($r < 1.5 \text{ nm}$, $V_0 < 0.5 \text{ cm}^3 \text{ g}^{-1}$, the magnitude of S_s is meaningless in this case), mesopores or transient pores ($r = 1.5\text{--}30 \text{ nm}$, $V_t \approx 0.8 \text{ cm}^3 \text{ g}^{-1}$, $S_s = 700\text{--}900 \text{ m}^2 \text{ g}^{-1}$), and macropores ($r > 30\text{--}6500 \text{ nm}$).

There are two basically different modes of the matrix isolation of nanoparticles. The first one is the most usual and consists in mere addition of a suspended or solubilised polymeric stabiliser to a prepared dispersion of particles (a modification of microencapsulation). There are other versions of this technique including mixing of metal powders with latexes. Latex is mixed with the metal phase particles having a size smaller than that of latex particles (100 and 700 nm, respectively) and, after the stabilisation of the resultant mixture (which is often accompanied by coagulation), the dispersive medium is removed. Then the coagulates are heated and moulded to produce samples of metal polymers.

‡ It is assumed that in most of the colloidal dispersions, the aggregation of particles leads to the formation of fractal clusters regarded as geometric objects possessing a self-similar structure in different spatial scales.⁵³

The second approach is based on the preparation of dispersions in the presence of a stabiliser or in the production of a stabiliser from its precursor in the presence of a prepared dispersion of nanoparticles. A widespread version of this method is the formation of nanoparticles in a polymeric medium. This makes it possible to prepare compositions in which the mixing occurs prior to the resin solidification.⁸ The materials produced are remarkable not only for the most uniform distribution of metal particles over the polymer bulk but also for strong chemical interaction of the metal with the polymer. On rare occasions, both components, *viz.* polymeric stabiliser and nanoparticles, are prepared *in situ*.

The complete stabilisation of nanoparticles by polymers is achieved when the adsorption–solvation layers are structured and form a structural–mechanical barrier for coagulation. The strength of these structures and their ability to recover rapidly after damage determine basically the aggregative stability of nanoparticles.

Now let us consider the most interesting techniques for the preparation of polymer-immobilised nanoparticles.

IV. Typical formation processes and the structure of nanometric metal particles in polymers

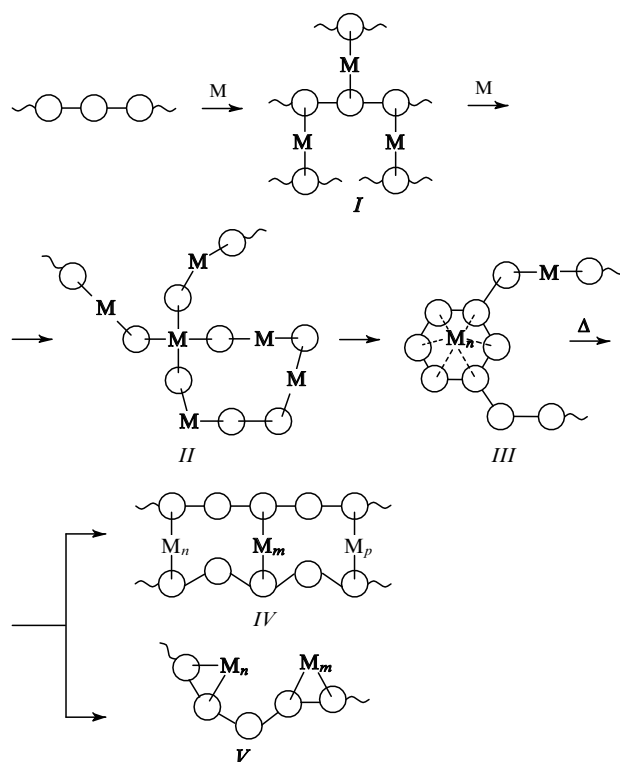
The difficulties of preparation and practical uses of polymer-immobilised nanoparticles are due, on the one hand, to a rather poor reproducibility of many synthetic procedures and, on the other hand, to rapid oxidation of particles of non-noble metals by potential oxidants at the stage of colloid formation. Virtually all of the known methods for producing polymer-immobilised nanoparticles are at least two-stage processes: they include molecular dispersion (atomisation or reduction) and subsequent condensation of atomic metal into nanoparticles. These stages occur in a rapid succession and virtually form an integral complex process of the appearance of nuclei and growth of a solid metallic phase. The very notion of 'solid phase nucleus' is somewhat equivocal. A cluster containing 25 Pt atoms corresponds in its adsorptional properties to a bulk metal.⁵⁶ On the other hand, in the course of gold chloride reduction, the collectivised ionic groups start to display properties characteristic of the metal nucleus (embryo) only after the accumulation of 300 and more Au atoms.⁴⁶

The heteroadagulation of polymer-immobilised nanoparticles on polymeric powders, films, or fibres could be the simplest method for their preparation. These studies have been carried out mostly on mineral supports, though there are also reports on heteroadagulation of non-stabilised hydrosols (8–12 nm) and organosols (4–11 nm) of Fe, Zn, and Cu on the surface of Dacron (lavsan) and polycaprolactam (capron) fibres.⁴⁰ On the lavsan fibres, the heteroadagulation rate is higher, which is explained by the specific interaction and the formation of the surface M–O bonds. The lowest adagulation rate is characteristic of the iron sol. However, the materials thus obtained are heterogeneous: the nanoparticles are localised only on the surface of polymers.

1. Technique of the atomic metal evaporation

The most attractive, from the technological viewpoint, are the methods of cryochemical deposition (most frequently, vacuum deposition at pressures of 10^{-1} – 10^{-4} Pa) of atomic (gaseous) metal on thin (~ 1000 nm) polymeric supports. The latter are usually high-molecular-weight paraffins, polyesters, oligo- and polyolefins, polydienes, vinyl- and phenyl-siloxane polymers. The metal atoms are first deposited at temperatures of 77 K and above (the so-called technique of 'bare' atoms).^{57–64} Then, the stabilisation of small clusters stable at low temperatures is carried out. In

Scheme 1

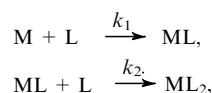


these systems, both homo- and heterocluster particles are formed and stabilised at an evaporation rate of 10^{-8} mol min⁻¹. As shown in Scheme 1, first a single metal atom forms bonds with two functional groups (arene rings, or oxygen atoms) (stage I). This is followed by the stage of metal–polymer chain 'growth' (II), and finally the stabilisation of clusters by ligands takes place (III). The stabilisation may also result from the inclusion of clusters into a trap of highly viscous metal–polymer network (IV) and the enlargement of cluster particles (V).

As a rule, the deposition results in the formation of mini-clusters, the size of which depends on the conditions of process and the nature of the metal (in most cases, transition metals are used). Cr clusters contain 2–3 metal atoms, those of Mo contain 2–5 metal atoms, and clusters of other metals include not more than 10 atoms.[¶]

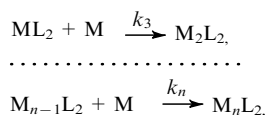
In principle, the kinetics of metal vapour condensation is analogous to the coagulation kinetics of an ideal suspension, which is in an absolutely unstable state, and which can be described by the Smoluchowski equation of fast coagulation.

Some spectral techniques have been elaborated for the identification of polymer-immobilised clusters. For example, mono-, di-, and tri-mers of molybdenum immobilised on poly(methylphenylsiloxane) absorb at $\lambda_{\max} = 318, 418,$ and 502 nm, respectively, whereas the four- and five-nuclear formations absorb at $\lambda_{\max} = 598$ and 640 nm, respectively. This makes it possible to follow the growth of cluster particles. According to Scheme 1, this process comprises a number of consecutive irreversible bimolecular reactions:



¶ These formations are thermally stable only below 290 K and disintegrate rapidly under the action of oxygen (even under a pressure of 1 mm Hg). Note for comparison that the energy of Cr–Cr and Mo–Mo bonds are 150 and 400 kJ mol⁻¹, respectively.

§ An interesting variant consists in the vulcanisation of rubber mixtures containing ferrite dust.⁵⁵



where M is a metal and L is a ligand.

The formation of clusters may be regarded as a continuous deposition of metal atoms on a polymeric film over the time t at the rate W ; then the corresponding rate equations are

$$\frac{d[\text{M}]}{dt} = W - \sum_{j=0}^p k_m[\text{M}][\text{M}_j\text{L}_2],$$

$$\frac{d[\text{M}_n\text{L}_2]}{dt} = k_m[\text{M}]\{[\text{M}_{n-1}\text{L}_2] - [\text{M}_n\text{L}_2]\}.$$

The concentration of cluster nuclei M_nL_2 of various nuclearity on the polymer may be expressed in general form as

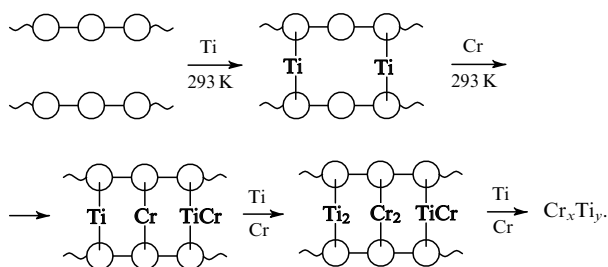
$$\frac{[\text{M}_n\text{L}_2]}{[\text{ML}_2]} = [\text{M}_0]^{n-1} \frac{2^{n-1}}{n[\text{L}_0]^{n-1}} = k[\text{M}_0]^{n-1},$$

where M_0 is the total mass of metal atoms deposited on the polymeric film over the time t .

Generally speaking, the cryochemical condensation of metals on cooled matrices leads to the formation of a variety of 'cluster series', which are interpreted⁶⁵ as a set of clusters with the monotonically increasing nuclearity with the same composition of ligands (M_nL_m , where $n = qx$, x is the nuclearity of the simplest member of this series, q is an integer). In these series, the basic structural elements (the simplest building blocks) are individual metal atoms, whereas the series *per se* are models of the atom-by-atom growth of metal particles. One can follow the course of their formation *via* the addition of individual 'bricks', which are elements of the nucleus formation.

It is significant that the cryochemical method allows the preparation of both homo- and hetero-metallic polymer-immobilised cluster particles. Thus the consecutive or simultaneous deposition of vapour of different metals, *e.g.*, Mo and Ti or Ti and Cr, especially at high concentrations, yields the non-solvated bimetallic clusters M_x^1M_y^2 , which are close in size to the colloidal particles (Cr_xTi_y) (Scheme 2) or to small clusters (the cluster Mo_xTi_y includes 13 atoms).

Scheme 2



The particles formed are chemically bound with the polymer and possibly bring about the cross-linking of its chains.

Control of the conditions of metal evaporation also allows the preparation of polymer-immobilised nanoparticles. For example, colloidal silver was obtained with the particle size of 1.0–20 nm (the colloidal Ag particles less than 40 nm in diameter absorb light at ~ 400 nm).⁶⁶ The dispersion of gold nanoparticles (mean particle size ~ 2 nm) in poly(diphenylbutadiyne) has been obtained by cocondensation of vapour of Au and diacetylene monomer on a support at 77 K.⁶⁷

Different versions of cryochemical synthesis have been developed using the protective properties of polymers. To this end, for example, an oscillatory contour is applied for the electrical condensational dispersion of metals.⁶⁹ In non-polar media, dispersions of Ag, Al, Bi, Cd, Cu, Co, Mo, Fe, Ni, Zr, Pt, Sn, and W with the particle size of 1–10 nm are stable only in the

presence of stabilisers (the synthetic rubbers SKD, SKB-35) that can form three-dimensional structures in solution. In their absence, immediate coagulation takes place.

The evaporation of solid polymeric particles (accompanied by considerable pyrolysis) and the co-deposition of volatile products (mostly radicals) with the metal vapour are used less often. This technique is employed, *e.g.*, for the formation of copper islets of ~ 10 nm in diameter in a polyethylene matrix.⁷⁰ The explosive evaporation of a metal wire coated with a polymer, when a short-circuit causes an instantaneous evaporation of metal and the fragmentation of polymer,⁷¹ processes of pulsed mechanochemical interaction (of the Bridgman anvil type),⁷² *etc.* are the modifications of this method. Over the recent years, a keen interest has been shown in the ionic spray of metals on polymeric surfaces. In this context, it seems appropriate to mention the studies into the vacuum deposition of Au and Zn on PE and PTFE.⁷³

The low-temperature condensation of Cr vapour with macromolecular matrices containing aromatic rings (oligobenzyl, oligoarylene, benzene-*m*-xylene copolymer) was used for the preparation of macromolecular sandwich-type Cr complexes.⁷⁴ The direct interaction of atomic metal with the matrix is prevented by the joint condensation of the metal vapour and the solvent (*e.g.*, chromium and diglyme).⁷⁵ This interesting technique makes it possible to replace the direct metal–matrix interaction by the process of exchange of one stabilising ligand for another high-molecular-weight ligand (this procedure is called resolution). Non-ionogenic surfactants are sometimes used for the replacement of dispersive medium. Thus the organosols of silver with particles 3–12 nm in diameter obtained by the cryochemical method in acetone are subsequently stabilised with 0.2% Triton X-100 solution in water and incorporated into a cross-linked polyacrylamide gel.⁷⁶ The nature of the solvent⁶⁴ and the polymer used for the cryochemical synthesis substantially affects both the reaction direction and the stability of products.

Resolution may precede the preparation of polymer-immobilised nanoparticles. For example, the cryochemical synthesis of colloidal Ag particles is performed in acetone, which is then replaced by formamide. Such a dispersion remains stable for a few days. The system Ag (2–5 nm)–formamide is used as a solvent in the preparation of cross-linked polyacrylamide gel.⁷⁷ Three different resolution variants for the synthetic purpose are documented.⁷⁸ In the first version, a Co–nonadecane system obtained by the cryochemical method was mixed with a solution of a polymer in nonadecane with subsequent sonication. In the second version, the nanoparticles of Co or Ni in toluene were added to a solution of low-pressure polyethylene (LPPE) in toluene at 363 K. Finally, according to the third variant, a toluene solution of a polymer was cooled from 383 to 185 K, and the gel-like system was mixed with nanoparticles obtained cryochemically and subjected to sonication. The above techniques make it possible to virtually preclude the aggregation of particles at all intermediate stages. However, along with the peptisation and resolution, more complex physicochemical interactions of nanoparticles with the solvent may also take place.

In the preparation of polymer-immobilised nanoparticles, the matrix, as a rule, does not remain indifferent to the fixation of metal atoms. This is often accompanied by a sharp decrease in the molecular weight of polymers (in particular, in the case of oligoarylenes)⁷⁵ or by the matrix structuring leading to the loss of solubility. In some instances, the ester and other bonds are cleaved, while the interaction of the functional groups of the polymer with metal atoms yields new products (*e.g.*, the splitting of the terminal chlorine atoms in the oligobenzyl matrix synthesised from benzyl chloride in the presence of Cr results in the formation of CrCl_3). The interaction of atomic zinc with the polymer surface is accompanied by a profound destruction of the polymeric subsurface layers and the interaction of zinc with the degradation products.⁷³

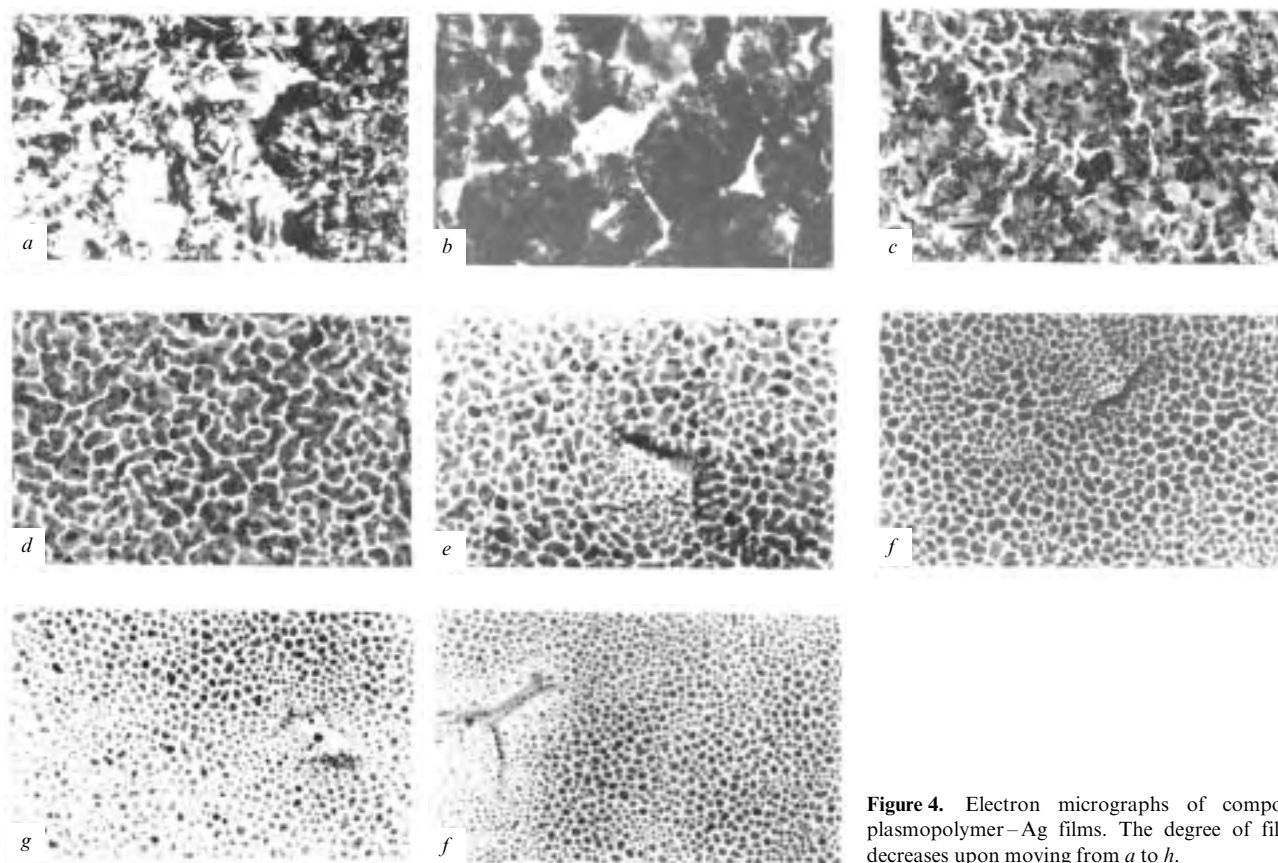


Figure 4. Electron micrographs of composite plasmopolymer–Ag films. The degree of filling decreases upon moving from *a* to *h*.

2. Preparation of polymer-immobilised nanoparticles by polymerisation in plasma

Polymerisation in a plasma (in a glow discharge) is initiated by ions, excited molecules, and photons with sufficiently high energy. The vapour pressure of a monomer (its concentration) during polymerisation in plasma is too low (10^{-3} – 10 mm Hg) to allow the production of polymers by the conventional technique. The role of polymer-forming substances is played by relatively simple compounds (CH_4 , CF_4 , benzene, chlorobenzene, perfluoropropane); less often, by more complex compounds. For example, homogeneous coatings enriched in beryllium are prepared by the thermal evaporation of Be with the concomitant deposition of a plasmopolymer of *trans*-but-2-ene.⁷⁹ In this method, mixtures of gaseous monomers with argon are often used. The chain mechanism of the polymer growth does not play a substantial role in the deposition of polymers from the gas phase. The chain propagation occurs basically according to a rapid stepwise mechanism with the predominance of reactions between active particles, which are often called reactions of polyrecombination. Although the products formed are regarded as polymers, they have however little in common with the usual materials of this type because of their structural peculiarities. As a rule, they are three-dimensional products with a high degree of cross-linking, especially when produced by extended (5–10 min) treatments with plasma. In the course of plasma-induced polymerisation, two competitive processes take place: the formation of a polymer by deposition from the gas phase and the etching (destruction) leading to its removal. The relationship between these processes at each specific site is determined by the energy of excited particles, their concentration, and the surface temperature, as well as by the nature of the monomer (*e.g.*, polymerisation predominates in the case of C_3F_8).⁸⁰

A substantial distinction of the plasma polymerisation from the traditional ways of polymer formation consists in the possibility of forming thin (50–100 nm), virtually defect-free films on most varied supports. It is also significant that the polymerisation

in plasma, is not restricted by the choice of material and the support shape. Therefore, this technique is well-suited for the preparation of microencapsulated nanoparticles (the so-called metal-doped polymeric films).⁸¹

Thin composite films are formed under the conditions of simultaneous polymerisation of corresponding compounds and vacuum evaporation of metals. Various modifications of this method[†] have been reported that differ basically in the mode of preparation and introduction of nanoparticles. One version of this method includes simultaneous evaporation of a monomer and metal from different sources,⁸⁵ while another relies on the combination of plasma polymerisation and metal evaporation.^{81,86} There is an original variant, according to which the plasma-induced graft polymerisation of monomers of traditional type (*e.g.*, vinylimidazole on a capron film)⁸⁷ occurs concomitantly with the metal evaporation. Of special interest is the plasma polymerisation of organometallic compounds.⁸⁸ The plasma-induced polymerisation of diethylberyllium is remarkable for the simplicity of the equipment required.

The preparation of polymer-immobilised nanoparticles most often involves combined targets including a metal and a polymer.⁸⁹ The target material is sprayed by plasma, and the sprayed product is deposited, as a rule, outside the plasma zone. It is very convenient to use the cathode material (Mo, Cu, Au) as the source of the metal. In trifluoropropane–metal systems thus obtained the content of the metal in the thin-film material amounts to 18 mass %–26 mass %. Metallopolymers with the formal composition $(\text{C}_3\text{F}_4\text{O}_{0.6}\text{Mo}_{0.3})_n$ and $(\text{C}_3\text{F}_3.9\text{O}_{0.3}\text{Cu}_{0.3})_m$ have been prepared and characterised.⁸² An aluminium-containing material with enhanced adhesion properties is produced by the spray and polymerisation of CH_4 in plasma using aluminium as the electrode

[†] The conditions of low-temperature plasma generation and the technology of plasmachemical processes are described.^{82–84}

material. Even at a relatively low frequency (10 kHz), the electrode surface is bombarded so strongly that the physical spraying of Al takes place with its inclusion into the growing macromolecule, the metal atoms being uniformly distributed over the bulk of the deposited material.

The volume portion (or the filling factor) of the metal embedded into the metallopolymeric material is calculated by the equation⁹⁰

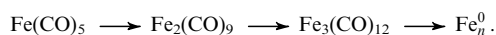
$$r = \frac{S_f - C_f}{S_m - C_f},$$

where S_f is the density of the metal-containing film, C_f and S_m are the densities of the 'metal-free film' and the metal, respectively. Depending on the conditions, the parameter r may vary from 0.1 to 1.0 reflecting the structure of the polymer-immobilised nanoparticles. Thus at low r values and short plasma treatments, the plasma polymerisation of benzene with silver yields quasi-two-dimensional particles.⁹¹ Their distribution pattern in the polymer depends on both the conditions of plasma polymerisation and the filling factor. For example, the transmission electron microscopy has shown⁹² that the composite plasmopolymer–silver films include three different structural regions with different r values (Fig. 4): the metallic region (a, b) composed basically of the metal particles with polymer inclusions, the percolational region (c) in which there are no aggregated metal particles and the formation of interacting cluster particles is initiated, and finally the region of the cluster particles completely isolated by the polymer ($d-h$), i.e., microencapsulated polycrystalline silver particles. Similar structure is characteristic of the Cu, Au, and Ag particles of colloidal size encapsulated with thin shells.^{93,94} This group also includes the particles of Au,^{80,81,95–97} Co, Al, and Mo⁹⁸ in fluoropolymers, Cu in polyethylene,⁸⁵ Ag in a polymer obtained from chlorobenzene⁸⁶ and benzene,⁹¹ etc. The distribution of gold nanoparticles in a polymer resulting from the plasma treatment of the C_3F_8 –Au mixture has been studied in detail.^{80,90} The mean size of gold particles is 5.5 nm ($r = 0.15$). The size of silver crystallites in thin composite films formed upon polymerisation of chlorobenzene and vacuum evaporation of Ag ranges from 5 to 10 nm⁸⁶ and from 100 to 200 nm at high Ag levels. Special studies have shown that neither AgCl nor silver carbide are formed.

Thus, the polymerisation in a glow discharge makes it possible to produce thin polymeric films of controlled size on the surface of nanoparticles prepared *in situ*. The complexity of this technique resides in the fact that it is difficult to control the rate of metal spray and its incorporation into the polymer formed.

3. Preparation of metal sols in polymers by the thermal decomposition of precursor compounds

Heating of volatile metal compounds (primarily, carbonyls, π -allylic complexes, formates, acetates, and organometallic compounds) in organic media or in the gas phase leads to their degradation with the liberation of metals or their oxides in the form of dispersed phase. An example is the decomposition of iron pentacarbonyl:

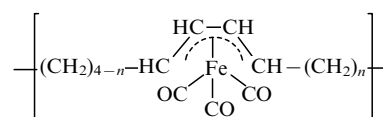


If these reactions are carried out in the presence of polymers, it is the simplest and apparently the most widespread method for the introduction of large (sometimes up to 90 mass %) quantities of colloidal particles of pure metals into polymeric compositions. This method underlies numerous processes intended for the preparation of polymer-immobilised ferromagnetic nanoparticles *via* the chemisorption of macromolecules on metal particles formed *in situ*. In the first place, this is pertinent to the thermolysis of metal carbonyls.

The stable homogeneous polymer-immobilised dispersions of colloidal particles of Fe, Co, Cr, Mo, W, Mn, Re, Ni, Pd, Pt, Ru, Rh, Os, and Ir can be produced using two modifications of the thermal decomposition of their precursor compounds.^{99,100} The first version is based on the use of solution of 'active' polymer

(containing amino, amide, imine, nitrile, hydroxyl, and other functional groups) in an inert solvent to which labile metal compound is added gradually. In this case, favourable conditions are created for the chemisorptional polymer–metal interaction. After this, the thermal decomposition is performed (mostly, at 100–170 °C). Sometimes the solution or suspension is subjected to different types of irradiation. The second modification relies on a 'passive' polymer that can react with the initial metal complex after the loss by the latter of at least one ligand (the CO group in the variant under discussion). The gradual addition to the solution of such polymers (*e.g.*, polystyrene, polybutadiene, co-polymers of styrene and butadiene, *etc.*) in an inert solvent of the initial complex at a definite temperature is accompanied by the dissociation of a ligand and the binding of the anionic complex with the passive polymer. Then the thermal degradation is performed.

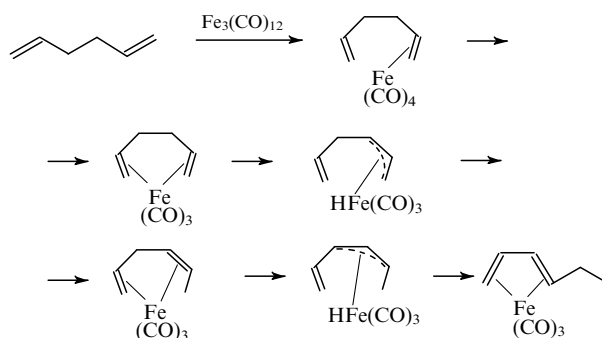
Certain stages of this multistage process (especially the particle growth) have much in common with the above-discussed transformations taking place during the condensation of metal vapour on polymeric matrices. One of the best studied processes is the thermolysis of cobalt carbonyl^{101,102} and iron carbonyl^{99,102–104} in the presence of polymers. For instance, the thermolysis of $Fe(CO)_5$ in a xylene solution of *cis*-polybutadiene or a block-copolymer of styrene and butadiene (408 K, 24 h, under argon) involving a number of consecutive stages leads to the formation of $[C_8H_{12}Fe(CO)_3]$ units:



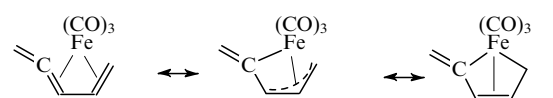
$n = 1, 2, 3.$

The initial stage involves the formation of a highly reactive anion $Fe(CO)_4^-$, which interacts with isolated double bonds, and then the isomerisation of double bonds occurs accompanied by the formation of π -complexes with the iron tricarbonyl residues. The final product is composed of the η^4 -(butadienyl)irontricarbonyl units with the *trans-trans*- and *cis-trans*-tetramethylene groups. Since the iron tricarbonyl complexes with two non-conjugated double bonds are unstable, no intermolecular products are formed. The reaction of iron carbonyls with low-molecular-weight non-conjugated dienes is accompanied by the double bond migration (Scheme 3).¹⁰⁵

Scheme 3



Three resonance structure are formed on the reaction of iron carbonyl with vinylallenes:¹⁰⁶



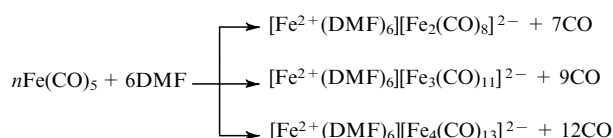
A characteristic feature is that the carbonyl complexes of the same type bound with the allyl fragments of the polymeric chain were also detected upon immobilisation of $Co_2(CO)_8$ or $Fe_3(CO)_{12}$ by the polystyrene–polydiene block-copolymers.^{107,108} The thermal decomposition of these polymer-immobilised π -allyl complexes

results in nanoparticles. In the case of polystyrene, the $\text{Cr}(\text{CO})_3$ fragments are bound to π -complexes with the benzene ring.¹⁰⁹

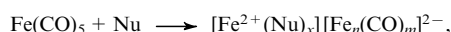
The size of nanoparticles depends on numerous factors, of which the major are the nature of the polymer-disperser, its molecular weight ($M \approx 100\,000$ is the optimum value), the nature of the functional groups (L), and the solvent. Thus under the conditions of annealing in vacuum at 493 K for 2 h, the cobalt-containing polystyrene–polybutadiene copolymer forms a non-magnetic phase of cobalt clusters ~ 1 nm in diameter, whereas the thermolysis at 473–573 K leads to the formation of particles with the size of 3–10 nm. Further increase in the thermolysis temperature up to 623 K leads to the enlargement of cobalt nanoparticles to the size of 50 nm and the appearance of the ferromagnetic properties in the materials formed.

The nature of the solvent plays a very important role. Metal carbonyls disproportionate in basic solvents (e.g., in DMF) to form complexes of ionic type in which metal atoms have the formal charge 2+. The composition of products identified by IR spectroscopy was found to depend on the ratio of the components (the extent of the substitution of carbonyl groups) (Scheme 4).

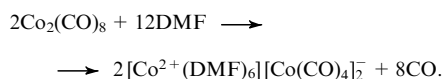
Scheme 4



In the general case:



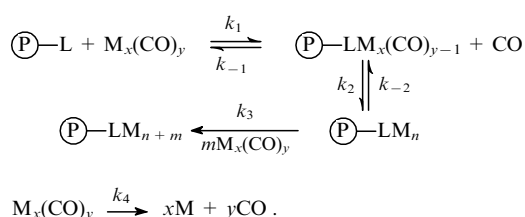
where Nu is a nucleophile (Py, *N*-methylpyrrolidone, etc.), $x = 2-6$; $n = 2, m = 8$, or $n = 3, m = 11$, or $n = 4, m = 13$. Under these conditions, dicobalt octacarbonyl is transformed according to the scheme



Basic solvents and high temperatures favour the binding of metal carbonyls by polymers. Stable colloidal dispersions are formed (e.g., iron dispersion with 5–10-nm particles) upon the thermolysis of carbonyls in dilute polymeric solutions. The nanoparticles of this type are very reactive, the particles with the size less than 10 nm are superparamagnetic, while the magnetic hysteresis is observed for the particle size of 10–20 nm.¹⁰⁴

The size of Co particles may be controlled within the range from 2 to 30 nm with a narrow interval of size distribution by varying the reaction temperature, the concentration of reagents, and the polymer composition (e.g., ter-copolymer of methyl methacrylate–ethyl acrylate–vinylpyrrolidone)¹⁰² in a solvent medium with low dielectric constant (e.g., in toluene). It is also noteworthy that the polymers containing larger number of polar groups can form particles of a smaller size. The same result is achieved by the decrease in the metal carbonyl concentration in the polymer.

The nucleophilic fragments of macroligands (in particular, those in the copolymer of styrene with *N*-vinylpyrrolidone) catalyse the degradation of metal carbonyls according to the scheme⁹⁹



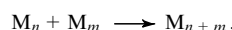
The first stage involves the ligand functional groups to form a soluble macromolecular complex, which by releasing CO is transformed into a polymer-immobilised cluster particle M^0 . The subsequent growth of this particle leads to the formation of a nanoparticle. As the matter of fact, there are stages of initiation, growth of particles, and the reaction termination, which may be regarded as a simple disproportionation of metal carbonyl on the particle surface.

The major requirement for the functionalised polymer consists in that the reaction rate on the polymer should be higher than the metal carbonyl decomposition rate in solution, i.e.

$$k_1 + k_2 - k_{-1} - k_{-2} > k_4,$$

$$k_3 > k_4.$$

Thus, in the thermolysis of metal carbonyls in polar media, as a rule, two major reaction routes are realised. First, the disproportionation products react with the polymeric chain and initiate the side reactions of cross-linking, destruction, and isomerisation of the chain, as well as the immobilisation of mononuclear carbonyl complexes. For example, the polybutadiene containing 92% of *cis*-1,4-; 4% of *trans*-1,4-; and 4% of 1,2- units ($M_r = 246$ kDa) if reacted with $\text{Fe}_3(\text{CO})_{12}$ for 2 h at 350 K undergoes isomerisation resulting in an increase in the content of *trans*-1,4 units up to 76%.^{103,110} Second, in parallel, there occurs major process of particle growth (enlargement) from the 'hot' metal atoms and the formation of nanoparticles with a size of 1–10 nm:



The binding of small, insufficiently grown particles (M_n) by the polymer



(in fact, the chain termination) leads, as a rule, to the formation of non-magnetic materials. Introduction of large (compared to the interchain distances and the size of crystalline blocks and cross-links) metal particles results in the perturbation of the polymer structure and deterioration of its physicomechanical properties. The reactions occur spontaneously along both routes, while the competition between them determines the ratio between the rates of thermolysis and diffusion towards the 'hot' metal centres in the solid polymeric matrix, depending on the nature of the reacting particles and the reaction conditions. In addition, these processes are considerably influenced by the character of the medium (oxidative or reductive).

The conditions of thermolysis of metal carbonyls in polymeric matrices and the size of nanoparticles thus formed are given in Table 1.

There is an original method for the formation of metallopolymers by localisation of particles resulting from the rapid unimolecular degradation of solutions of metal compounds in molten polymers, in natural cavities of polymeric matrices of polyethylene, polypropylene, polytetrafluoroethylene, etc. These materials were given a collective name of Claspol.^{112–115} In this process, the melt temperature should considerably exceed the temperature inducing the degradation of carbonyls. Carbonyls are used as dilute solutions under conditions providing for the most rapid and complete removal of ligand from the reaction system. This technique offers a number of advantages. On the one hand, higher temperatures increase the extent of carbonyl decomposition and reduce the yield of by-products, on the other hand. In addition, in contrast to solutions, the melts preserve the close order of the initial polymer structure, while the cavities may host the particles formed. The polymer-immobilised particles thus obtained are characterised by a relatively high dispersity and homogeneous distribution over the polymer volume, while macromolecules are irreversibly sorbed on their surface. The metal particles are

Table 1. Thermal decomposition of metal carbonyls in polymeric matrices.

$M_a(\text{CO})_b$	Polymeric matrix	Conditions of thermolysis	Content of nanoparticles (mass %)	Size of nanoparticles /nm	Ref.
$\text{Co}_2(\text{CO})_8$	Without polymer	Toluene		> 100	101
	Copolymer MMA – vinylpyrrolidone (90:10)	Chlorobenzene	75	6–25	101
	Polychloroprene	Toluene	93	30–60	101
	Copolymer vinylchloride – vinylacetate – vinyl alcohol (91 : 6 : 3)	Chlorobenzene	75	7–47	101
	PS	Toluene	75	10–30	101
	Copolymer styrene – acrylonitrile (88 : 12)	"	75	6–13	101
	Atactic PP	"	75	> 100	101
	Polyesters	"	75	6–20	101
	Polyurethane	"	75	5–30	101
	Tercopolymer MMA – ethyl acrylate – vinylpyrrolidone (33 : 66 : 1)	"		20–30	102
$\text{Fe}(\text{CO})_5$	Polystyrene – block-polybutadiene	Dichlorobenzene, 145 °C		7–8	99
	Polybutadiene	Decalin, 140–160 °C		5–15	99
	<i>cis</i> -Polybutadiene	Xylene, 135 °C			118
	Polybutadiene	Decalin, 150 °C		~6	104
	Copolymer styrene – butadiene (5.8 : 1)	Decalin, 150 °C		~6	104
	Copolymer styrene – 4-vinylpyridine (1 : 0.05)	<i>o</i> -Dichlorobenzene	2	~6	104
	The same (1 : 0.1)	<i>o</i> -Dichlorobenzene	1.8	~16	104
	Polyvinylidene fluoride	DMF, 140 °C		5–15	104
	<i>cis</i> -Polybutadiene	1% solution of dioxane – xylene, 135 °C,	37		93
	Natural rubber	8% solution of dioxane – xylene, 125 °C	17		103
$\text{Fe}_3(\text{CO})_{12}$	<i>trans</i> -Polybutadiene	Benzene, ethanol, 80 °C	23		103
	Copolymer styrene – butadiene (25 : 75)	Benzene, 80 °C	8		103
	Polybutadiene (81% repeat 1.2-chains)	Benzene – dimethoxyethane, 80 °C	16		103
$\text{Fe}(\text{CO})_5$	PE melt	–	1–29	1.5–7	112–114
	PP (isotactic, melt)	–	5		112–114
	PP (atactic, melt)	–	5–30		112–114
$\text{Cr}(\text{CO})_6$	PTFE (fluoroplast-40), melt		0.5–4	1–5	112–114

primarily localised in the amorphous, less compact matrix regions. This renders difficult the segmental displacement of the amorphous phase resulting from both the reduced free volume and its possible cross-linking. The polymeric materials formed display enhanced thermal resistance (*e.g.*, in the case of atactic polypropylene modified with metal clusters, T_m is increased by 50–80 °C) and the product acquires a monolithic pseudocrystalline structure. The recurrent spacing of the distribution of metal clusters in it is concentration-dependent and in the case of iron, for example, is 9–12 nm at high concentration (20 mass %–30 mass %) and 20–22 nm at low concentration (2 mass %–3 mass %) with a narrow size distribution of particles (half-width ~1 nm). It is significant that the presence of the metal phase does not affect either chemical or physicochemical properties of such materials as the strong interaction of nanoparticles with the polymer leads to the formation of pseudocrystalline materials. In other words, at definite ratios of ingredients, these products are one-phase metal-polymers.

Of particular interest is the thermolysis of metal carbonyls in the halogen-containing matrices, which apparently should be

regarded as ‘passive’ in terms of the above-discussed classification. The modification of PTFE by Fe^{3+} or Mn^{4+} oxides is brought about by the sorption of the corresponding carbonyls and their subsequent decomposition under the action of KMnO_4 or H_2O_2 .^{116–118} The oxides formed are incorporated into the amorphous regions of PTFE.

In most cases, nanoparticles are prepared in polar solvents that form intermediate complexes with the carbonyls (see Scheme 4), which react with the fluorinated polymers. The main factors influencing the selectivity of the $\text{Fe}(\text{CO})_5$ or $\text{Co}_2(\text{CO})_8$ reaction with polyvinylidene fluoride (PVF) in the course of their thermolysis have been discussed.^{119–121} The results of IR spectroscopy indicate that the adsorption leads to the formation of complexes $[\text{Fe}^{2+}(\text{DMF})_6][\text{Fe}_3(\text{CO})_{11}]^{2-}$ – PVF and $[\text{Co}^{2+}(\text{DMF})_6][\text{Co}(\text{CO})_4]^-$ – PVF, and made it possible to carry out kinetic studies and to elucidate the mechanism of their degradation. The thermolysis of both intermediates follows the mechanism of first-order reactions; however, the rate constant and the activation energies of these processes are substantially different (Table 2). The thermolysis rate constant of polymer-

Table 2. Reaction rate constants and activation energy of decomposition of different products in systems $M_x(\text{CO})_y$ -PVF (140 °C, DMF).¹²⁰

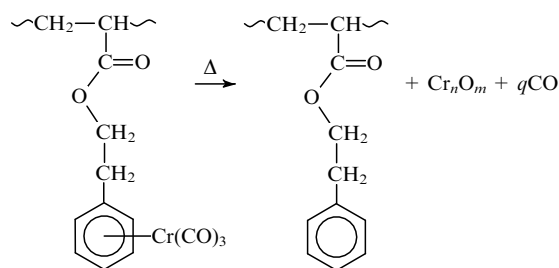
System	$10^{-5} k / \text{s}^{-1}$	$E_a / \text{kJ mol}^{-1}$
PVF-Fe(CO) ₅	8.41	142.59
PVF-Fe ₃ (CO) ₁₁ ²⁻	12.2	51.62
PVF-Co(CO) ₄ ⁻	104	45.80

immobilised cobalt carbonyl is one order of magnitude higher than that of iron carbonyl. This is consistent with the fact that the cobalt carbonyl anion is more reactive than the iron carbonyl anion. A very high activation energy of the decomposition of neutral Fe(CO)₅ in PVF compared with E_a for the immobilised carbonyl reflects differences in the mechanisms of these reactions. The thermolysis of Fe and Co carbonyls in PVF *in situ* leads to the formation of heterophase metallic domains in the polymeric matrix. When the same carbonyls are bound with the polymer, the homogeneously distributed ferromagnetic particles of 5–10 nm in diameter are produced. The mean surface area per particle varies from 80 to 700 nm². The electron diffraction analysis of these systems has revealed the formation of γ -Fe₂O₃ and FeF₂ particles from Fe(CO)₅, and of Co, Co₂O₃, and CoF₂ from Co₂(CO)₈.¹²⁰ The appearance of metal fluorides is associated with the involvement in this reaction of the polymeric chain with the cleavage of C–F bonds.

Hence, two parallel processes occur in these systems: the major process leading to the formation of nanoparticles upon the thermolysis and the side process, which consists in the attack of the polymer chain by metal ions and is accompanied by various transformations of the polymer itself (destruction, cross-linking, binding of metallocomplexes). Besides, the secondary carbenium ions formed from PVF (the formation of carbenium salts was also observed in the interaction of halides of transition metals with halogen-containing polymers)¹²² are highly reactive and take part in various reactions. Recently, the formation of ZnF₂ was reported⁷³ as a result of the reaction of atomic zinc with the PTFE surface.

The character of bonding the clusters and nanoparticles with the polymeric matrix and their topography have not been totally clarified to date; nonetheless, it is obvious that the reactivity of the metal centres formed in the course of decomposition is a critical factor controlling the character of interaction between the polymer and the metal particle.

In the thermal degradation (especially, in the oxidative atmosphere), immobilised polynuclear complexes[‡] with volatile ligands may form nanoparticles of metals and their oxides, and sometimes also with admixtures of metal carbides. Thus heating of poly(η^6 -phenyl methacrylate)-Cr(CO)₃ films at 423 K resulted in the formation of a mixture of chromium oxides enclosed in the matrix of a cross-linked polymer:¹²⁴



In a similar way, the thermolysis of copolymers of acrylonitrile or styrene with (η^4 -hexa-2,4-dienyl acrylate)iron tricarbonyl in air at 473 K leads to the formation of nanoparticles of Fe₂O₃.¹⁰⁹

‡ The fixation of mononuclear metal carbonyls on polymers⁴ and the synthesis of organometallic polymers¹²³ are reviewed.

The distinctive feature of nearly all polymers of this type is that they decompose without melting, apparently owing to the formation of cross-linked structures. Since the metal oxides are the final products of the oxidative decomposition of any metal-containing polymer, the possibility of the replacement of toxic Fe(CO)₅ by polyvinylferrocene¹²⁵ has long been debated.

Less often, the carbonyls, which act as metal-forming substances in the preparation of polymer-immobilised nanoparticles by thermolysis, are replaced by other precursor compounds, usually by metal formates, acetates, and oxalates,^{126–129} and by organometallic compounds. Recently, a metal–polymer composition of the ‘Claspol’ type was obtained by the thermolysis of a triethylenediamine complex of copper formate [Cu(En)₃]. (HCOO)₂ in PS using dimethylformamide as the common solvent.¹³⁰ This complex disintegrates at 170 °C to form metallic copper in a highly dispersed state. It is noteworthy that this temperature is 20 °C lower than that of the thermolysis of the initial copper formate, which is explained by the catalytic effect of the polymer on the thermal degradation of this complex. The point is that the reactive centres of the polymer favour the formation of metal particle nuclei, which are precisely the centres of aggregation. This is followed by the thermolysis and redistribution of the copper complex. The maximum quantity of copper that can be incorporated into PS is 10%.

PTFE increases the decomposition temperature of cadmium oxalate trihydrate,¹²⁶ while the products of degradation of the latter, in turn, increase the temperature at which an intensive degradation of PTFE begins. The thermal decomposition of the highly dispersed copper formate leads to the formation of a metal–polymer composition (20%–34% Cu); the maximum on the granulometric curve of nanoparticles corresponds to ~4 nm. No chemical interaction between the components was observed. The decomposition of a fine dispersion of palladium hydroxide in polyvinyl chloride (PVC) results in spatial structures with highly dispersed Pd particles ($S_s = 26 \text{ m}^2 \text{ g}^{-1}$) in the nodes.¹³¹ It is significant that this process results in the increase in the temperature of complete dehydrochlorination of PVC. The thermolysis of cobalt acetate in the presence of PS, PAA, and poly(methyl vinyl ketone) proceeds at a much higher temperature and leads to the formation of metal clusters that catalyse the electroreduction of oxygen.¹³²

The preparation of a highly dispersed Cd phase regularly distributed in the PS bulk by mixing PS with dibenzylcadmium in THF followed by removal of the solvent and decomposition of the organometallic compound at 130 °C has been reported.¹³³ Materials containing 1.4%–4.3% of metal were obtained from the bisarene complexes (C₆H₅CH₃)₂M, where M = Ni, Co, synthesised by the cryochemical method, by their rapid degradation in LPPE at temperatures higher than the complex decomposition temperature.⁷⁸ Cobalt nanoparticles (with the mean particle size of ~1.6 nm and narrow particle distribution) were prepared¹³⁴ by hydrogenation of the organometallic compound Co(η^3 -C₈H₁₃)(η^4 -C₈H₁₂) in the presence of PVPy at 273–333 K. An original method of impregnation of organometallic compounds into the amorphous regions of PS, high-pressure polyethylene (HPPE), PTFE, and polyacrylates followed by their structural modification and formation of clusters has been exemplified with cymanthrene (η^5 -C₅H₅)Mn(CO)₃.¹³⁵ To this end, fluids are used in their supercritical state (CO₂ under a pressure of 8–25 MPa at 30–40 °C).[§] According to another protocol,¹³⁹ a precursor, dimethyl(cyclooctadiene)platinum(II) is dissolved in CO₂, and the solution obtained is used to impregnate thin films of poly(4-methylpent-1-ene) or PTFE. The reduction of this system by thermolysis or hydrogenolysis yields polymer-immobilised nanocomposites with the Pt particle size of 15–100 nm.

§ The interest in the processes occurring in supercritical fluids has sharply increased over the recent years,^{136,137} especially in the reactions in supercritical CO₂.¹³⁸

Despite the abundance of studies of this sort, the relevant literature does not carry any information on the thermolysis in polymer-immobilised carbonyl-hydrides, substituted (mixed) carbonyls, and mixed metal carbonyls (such as $\text{Co}_2\text{Ir}_2(\text{CO})_{12}$, $\text{H}_3\text{FeRu}_3(\text{CO})_{15}$, $\text{Fe}_2\text{Ru}(\text{CO})_{12}$, or $\text{MM}'(\text{CO})_n$, where $\text{M} = \text{Mn}$, Re ; $\text{M}' = \text{Cr}$, Mo , W), *etc.* The data on the thermolysis of metal carbonyls in reactoplasts are also very meagre. The only thing known is that the heating of the degradable metal carbonyls introduced into an epoxy resin leads to the deposition of nanoparticles on the surface of the polymer formed.¹ Possibly, in this process the highly reactive metal particles initiate the opening of the epoxy ring with the formation of three-dimensional structures.

4. Reductive methods in the synthesis of polymer-immobilised nanoparticles

The reductive methods appear to be the most common techniques for the preparation of polymer-immobilised nanoparticles. They may be divided into two types different in principle. The first type, or the 'impregnation' method consists in the chemical reduction of metals from solutions or suspensions of their salts (to this end, ammoniacal solutions of Cu , Cr , and Ag hydroxides are often used) or in the electrochemical or radiation-chemical reduction in the presence of macroligands. The second type resides on the reduction of mononuclear metal complexes chemically bound with polymers. The first method is more widely applied because it meets better the needs of catalysis. In particular, metal blacks, ultradispersed powders, *etc.* are prepared thereby. For example, Raney nickel is stabilised by incorporating it into the silicone rubber¹⁴⁰ with the subsequent polymer vulcanisation at room temperature.[¶]

Sols of Au , Fe , and Cr were prepared by the reduction of their hydroxides by hydrazine hydrate in a matrix of water-soluble polymers, and dispersions of particles of Pd (1–2 nm) and Au (1–13 nm) were obtained in synthetic rubber films.¹⁴³ The treatment of polymeric films prepared from aqueous solutions of PVA and AgNO_3 with photographic reducing agents (hydroquinone, *p*-phenylenediamine, pyrogallol, *etc.*) yields the corresponding metallocomposite materials.¹⁴⁴ Monodispersed hyperfine powders of gold^{145, 146} and platinum^{147–149} were prepared by the reduction of their salts in the presence of protective colloids.

Natural polymers (gelatin, gum arabic, agar, proteins and products of their hydrolysis, sodium protalbuminate, starch, cellulose and its derivatives) and polymeric compounds soluble in organic media (synthetic rubbers, naphthenic acids) are often used as protective high-molecular-weight compounds in the production of sols of silver, mercury, bismuth, copper, and platinum group metals by the reduction of corresponding ions. β -Cyclodextrin may also be employed as a stabilising agent for colloidal particles of Rh , Pt , and Pd (1–100 nm).¹⁵⁰ Ultrafine particles of Ni (5–20 nm) were prepared by reduction with hydrogen of $\text{Ni}(\text{NO}_3)_2$ following the diffusion into gel membranes of cellulose acetate.¹⁵¹ It is significant that the adsorption of ions by protective polymers (see Section III) creates favourable conditions for the concomitant appearance of a large number of embryos (nuclei) of colloidal metal particles. The metal that is reduced is mostly consumed to form these embryos, while only small quantity remains for their growth. As a result, only small nanoparticles are formed, and this is also favoured by the high aggregative resistance of sols.

The radiation-chemical and photo-induced reduction is preferred to the reduction by hydrogen when it is necessary to prepare small particles with a narrow size distribution.¹⁵² A characteristic example is the preparation of 'blue silver' in the process of

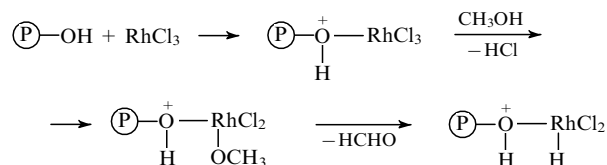
γ -irradiation of slightly alkaline aqueous solutions of AgClO_4 containing 2-propanol and PAA.⁴⁵ The 'blue silver' is a linear Ag cluster stabilised on a polymer molecule. In the course of radiation-chemical reduction, the Ag clusters are transformed through a number of successive stages into a polymer-immobilised colloidal silver.

The interaction of H_2 with colloidal Pd obtained by the radiation-chemical reduction of Pd^{2+} in an aqueous solution of PAA does not increase the particle size and is accompanied solely by hydrogen sorption on the surface of nanoparticles.¹⁵³

It is noteworthy that the 'impregnation' method does not rule out the chemical interaction between the compound to be reduced and the polymeric matrix. The absence of chemical interaction between the metal and the polymer is rather an exception than the rule. For example, in the systems based on polymers devoid of functional groups (polyacetylene and MX_n) the macromolecule plays the role of a specific ligand; this hampers the multicentre association of complexes and prevents their enlargement.¹⁵⁴ Most probably, the condensation of a metal in a liquid phase occurs at the moment when its ion undergoes reduction and not after the formation of a supersaturated solution of metal atoms. The formation of nanoparticle nuclei occurs spontaneously, basically at the sites of largest concentration of metal ions, whereas their growth results from the reduction of ions adsorbed on the surface. Apparently, this process has much in common with the growth of particles in the course of cryochemical synthesis.

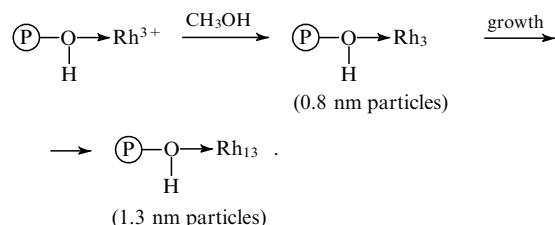
The mechanism underlying the reduction of metal ions chemically bound with polymers is rather complex. It has been elucidated in detail using the formation of clusters of zero-valent Pd , Ru , Rh , Ag , Os , Ir , Pt , Au , and Ni as the examples.^{155–158} When solutions of salts of these metals in proton-donating solvents are boiled in the presence of polymers (*e.g.*, a solution of RhCl_3 in aqueous methanol mixture in the presence of PVA), several chemical transformations take place (Scheme 5).

Scheme 5



At the first stage of this complex process, RhCl_3 coordinates with PVA, then an oxonium product is formed, which is further transformed *via* alkoxide into a polymer-bound hydride complex. These reactions lead to a homogeneous colloid resulting from the disproportionation of rhodium hydrides and subsequent growth of particles (Scheme 6).

Scheme 6



The 13-nuclear clusters formed have the structure of a face-centred cubic lattice with a rhodium atom coordination number equal to 12. The clusters are 4 nm in diameter. They interact with the protective polymer owing to electrostatic attraction or to physical adsorption, and possibly to the formation of coordination bonds.

By changing the reaction conditions, the nature of the medium, (ethanol, butanol, toluene–butanol), by introducing additional ligands (*e.g.*, PPh_3), or using various polymers (*e.g.*,

¶ Synthetic rubbers may also be vulcanised by salts of unsaturated acids; this results in the formation of vulcanised metallopolymeric structures.¹⁴¹ Metal–polymer compositions are prepared by introducing dispersed metal (Al , Fe , Cr , Ta , W) powders into oligomers, for example, into trioxoethylenedimethacrylate with subsequent solidification induced by a flux of accelerated electrons.¹⁴²

PVPr, copolymer of MMA with *N*-vinyl-2-pyrrolidone, polyacrylamide gel, *etc.*), one can prepare metallopolymers with cluster particles of different size (0.9–4 nm for Rh⁰ and 1.8 nm for Pd⁰). These particles are stable in the protective colloid, they have a narrow size distribution and high stability (they remain in the gel upon variation of pH from 2 to 12). Thus, the water-soluble polymers act in these systems as protective colloids, while alcohols play the role of reducing agent.

The reduction of NiCl₂ by NaBH₄ in ethanol in the presence of PVPr may be used for the preparation of nickel boride sol, it is still more suitable for the preparation of organosols of noble metals. It proved to be very useful in the synthesis of colloidal dispersions of polymer-protected bimetallic Pd–Pt or Pd–Au clusters.^{159–161} They were produced by the joint reduction of PdCl₂ and H₂PtCl₆ or HAuCl₄ in the presence of PVPr (by boiling in methanol or illumination with visible light). The products remained stable for a few months at room temperature. The size of Pd–Pt and Pd–Au clusters was ~1.5 and 3.4 nm, respectively. This method was also used to prepare the polymer-protected bimetallic Pt–Co colloids with Pt:Co ratios of 3:1 and 1:1.¹⁶²

The obstacle to the synthesis of metal colloids based on insoluble polymers is the diffusion of ions to be reduced into the polymeric matrix. For example, reduction of Ni²⁺ with NaBH₄ in aqueous methanolic solution in porous isotropic isotactic polypropylene (PP) has been carried out using the method of counter-current diffusion.¹⁶³ The process comprises the following consecutive stages: penetration of metal ions and the reducing agent into the polymeric matrix, in-depth diffusion of reagents described by the Fick's first law, and finally, the chemical reaction itself. The size of the nanoparticles formed depends on the reaction conditions and the parameters of the porous polymeric structure. This technique allows the microencapsulation, in the polymer pores, of metal crystallites (3–10 nm in diameter) assembled in polycrystalline aggregates with the controllable size of narrow distribution. Nickel particles prepared by the reduction in the polymeric matrix resisted oxidation in water for over two weeks, whereas when dried, it remained unoxidised for half a year.¹⁶⁴ At the same time, the nickel obtained in the absence of polymers rapidly oxidised in water and air. A mixture of reduced Ni with a polymer solution proved also to be unstable. Apparently, the shielding with polymers prevents not only further growth of particles but also provides their high resistance to oxidation. It is assumed that the macromolecules can trap and stabilise the nuclei of metallic phase owing to the cooperative interaction of chain segments according to the mechanism of matrix 'recognition' by the growing chain during the matrix polymerisation.¹⁶⁵

Under the action of different reducing agents, the immobilised complexes (including the mononuclear ones) may undergo different transformations leading to the increased nuclearity. For example, compounds of Rh, Ru, and Pt fixed by ion exchange on the completely fluorinated resin Nafion (Fig. 3) undergo reduction in a flow of H₂ at 473 K with formation of metallic clusters with sizes of 2.8, 3.3, and 3.4 nm, respectively.^{50,51,166} Cations of Ag, Cu, Rh, Ru, Pt, and Ir bound to perfluoroethylenesulfonic acid or to a partially sulfated PS oxidise CO, NO, NH₃, N₂H₂, and C₂H₂ at 373–473 K, and this process leads to the formation of metal particles 2.5–4.0 nm in diameter.¹⁶⁷

Generally speaking, the formation of polymer-immobilised metalclusters in the course of catalytic reactions is a rather common phenomenon, especially in complex organometallic catalysts deposited on polymers.^{4,168} This phenomenon may be the reason for both the activation of these catalysts (*e.g.*, in hydrogenation reactions) and their inactivation (in particular, in reactions of ionic-coordination polymerisation). Significant data on the transformations of immobilised Ni²⁺ in the course of ethylene dimerisation¹⁶⁹ were provided by measurements of magnetic susceptibility in strong magnetic fields (up to 70 kG) and low temperature (4.2 K).¹⁷⁰ Under these conditions, the susceptibility of different spin states depends non-linearly on the

magnetic field strength (described by the Brillouin's function), which made it possible to establish the distribution of nickel states over the magnetic moment values. Evidence has been provided for the formation of one-nm microparticles containing 10–30 Ni atoms that display no ferromagnetic (supermagnetic) properties and are polymer-immobilised clusters with ferromagnetic exchange. In the polymer-immobilised cobalt systems (the catalysts of butadiene polymerisation) a considerable proportion of Co²⁺ ions are reduced to the metallic state in the absence of polymerised monomer. In any case, 90% of total ferromagnetic cobalt is localised in the relatively large particles 10 nm in diameter.¹⁷¹

There are other numerous methods for the chemical reduction of metal salts in the presence of polymers yielding polymer-immobilised nanoparticles.

5. Electrochemical methods for the preparation of polymer-immobilised nanoparticles

The electrochemical and electroflotation methods are widespread techniques for the preparation of chemisorbed macromolecules bound to colloidal metal particles generated *in situ*. Reactions of electrochemical polymerisation are heterogeneous: they are initiated on the electrode surface, while other stages (chain growth or termination) occur, as a rule, in the liquid phase.¹⁷² The yield of a polymer depends on the chemical and physical nature of the electrodes and their surface, electrode overvoltage, potential under which the reaction occurs, and electrical current density. The nature of the electrode material (metals or alloys, thin metallic coats, *etc.*) determines the characteristics of electron transfer reactions (initiation) and polymerisation. Such types of electrode processes as direct electron transfer between the electrode and monomer, cathodic deposition and anodic solubilisation of metals are optimum for the electrochemical polymerisation. Metal salts, which are the precursors of nanoparticles, may act as specific electrochemical activators influencing the process through direct chemical binding to the monomer and by virtue of transfer, decomposition, or catalytic effect. Nonetheless, the method of electrochemical polymerisation has found only limited use in the preparation of polymer-immobilised nanoparticles.

A procedure for the preparation of metal organosols by electrolysis in a two-layer bath proved to be more suitable.^{1,2} The upper organic layer of the electrolytic bath is a dilute solution of a polymer in an organic solvent (sometimes, supplemented with a minor quantity of surfactant), which interacts near the interface with the nascent colloidal metal particles.

Less often, nanoparticles are formed on polymers by means of electrophoretic and electrochemical deposition of metals from solutions onto polymeric suspension that is used as an additive in the electrolysis.¹⁷³ The metallopolymer formation results from the polarisational interaction of polymer and metal particles during deposition on the electrode and the chemisorptional interaction of macromolecules with the surface of metal at the moment of its reduction. This process includes several stages, such as discharge of Mⁿ⁺ ions, crystallisation of deposited metal, a number of parallel electrochemical reactions, *etc.* The contributions from different stages depend on the concentration of the dispersed phase and electrolyte, and the particle charge. The ratio between these contributions determines the transition from polymer-immobilised nanoparticles to electrochemical plating with high metal content.

Owing to the shielding properties of polymeric particles, the surface of the electrode and metal particles is blocked, and a specific type of polarisation known as electrophoretic polarisation appears, which has an appreciable effect on the process of metal electrocrystallisation. The polymer is often deposited as a separate phase (liquid or solid) on the electrode surface. Therefore, the transfer of ions, electrons, or neutral particles through the layer of the new phase may face noticeable kinetic restrictions depending on the permeability of polymeric coating. Coating the anode with an insulating polymer layer reduces the electrode activity and the

current amplitude. This inconvenience can be partly eliminated by the use of liquid electrodes, *e.g.*, the dropping mercury electrode.

Let us consider some characteristic examples. Colloidal Pd particles are obtained by the electrolysis of aqueous solutions of palladium chloride at pH 1 in a two-layer bath in the presence of a hydrocarbon solvent and epoxy dianic resin or PVA.¹⁷⁴ Electrolysis results in the formation of organosols of colloidal palladium stabilised by the chemisorptional bonds of the polymer. The products remaining after the removal of solvent and residual electrolyte are metallopolymers containing up to 90%–95% of Pd. They are formed under high cathode polarisation with abundant concomitant elimination of hydrogen adsorbed on the nanoparticles (5.5–7.8 nm in diameter).

The combined deposition of Ni nanoparticles and PTFE suspension from the sulfamic-acid electrolyte for nickel-coating at room temperature leads to polymer inclusion into the Ni deposit (up to 20 mass %). The process is controlled by varying the cathode current density and the concentration of suspension introduced.¹⁷⁵ The relationship between the homo- and hetero-coagulation interactions of metal particles and polymer is determined by the rates of electrochemical deposition and isolation of metal in the Ni–PTFE systems.¹⁷⁶

In turn, the electrode material may become the precursor of nanoparticles of noble metals; polypyrrole films containing functional groups such as 4,4'-dipyridyl, alkylammonium, and others may serve as protectors in this case.^{177–180} Bimetallic Pd–Pt or Pd–Rh nanoparticles incorporated into such films are also used for the electrocatalytic hydrogenation.¹⁸¹ Fine dispersions of iron powders (~200 nm) formed electrochemically may be used as modifying coats of various materials.¹⁸²

Thus, the effect of polymeric dispersions on the reduction of metal ions depends on the concentration and composition of the electrolyte and the dispersed phase, charge and size of polymeric particles, and the mode of electrodeposition.

The thermal techniques have substantial advantages over the electrochemical ones because the latter occur with considerable degradation of the dispersive medium, noticeable oxidation of the colloidal particles formed, *etc.*

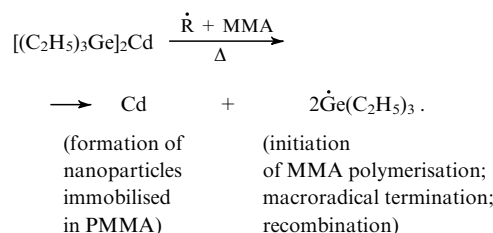
6. Preparation of polymer-immobilised nanoparticles at the polymerisation (polycondensation) stage

Of special interest are the methods including simultaneous formation of the matrix and nanoparticles. This large group of techniques is reported mostly in the patent literature. The early studies^{183, 184} have already demonstrated the ample possibility of initiating the polymerisation of vinylic monomers by intensive mechanical dispersion of certain inorganic substances, including metals (Fe, Al, Mg, Cr, W). The degree of polymerisation of monomers (styrene, vinyl acetate, acrylonitrile, MMA) depends on the dispersion intensity. The role of catalyst and initiator is played by freshly formed metal surfaces: they are the sites of electron transfer from the superficial metal atoms to the monomers to form initiating particles of ion-radical type. Colloidal particles of Au, Ti, and Pt were found to influence substantially the bulk and solution polymerisation of styrene.¹⁸⁵

Sometimes, organometallic compounds are used instead of compact metals in the preparation of polymer-immobilised nanoparticles. The addition of relatively small quantities of organocadmium compounds has virtually no effect on the initial rate of radical polymerisation of MMA.^{186–189} In this case, nanoparticles may be obtained by two routes: from organometallic compounds (*e.g.*, from bis(triethylgermyl)cadmium) that decompose at a temperature close to that of polymerisation or by heating the composition formed including a component whose decomposition temperature is higher than that of MMA polymerisation (*e.g.*, alkyl derivatives of cadmium). Interestingly, the organocadmium compounds of this type diminish considerably the molecular weight (M_n) of the PMMA formed. For example, its M_n decreases from 800 to 60 kDa in the presence of 2.5 mass % of these compounds. Chain transfer on the organometallic compound

may be probable reason. The formation of nanoparticles in the monomer–polymer mixture may be schematically represented as follows (Scheme 7).

Scheme 7



The size of Cd nanoparticles formed at the polymerisation stage increases as the content of the initial component in the monomeric mixture increases: from 6.3 nm at 8 mass % to 300 nm at 40 mass %. Compositions formed upon heating contain larger nanoparticles that have a regular hexagonal structure characteristic of Cd crystals.

In the processes under consideration, the critical parameters are the ratio of the rates of decomposition of the organometallic component and the polymerisation of the corresponding monomer, and the sedimentational resistance of metal dispersions formed in the monomer. Apparently, this also holds true for solidifying systems, for example, for the thermally generated epoxy-thiocol resin, into which colloidal Pb is incorporated at the moment of its formation by thermolysis.¹⁹⁰ In this case, however, one should also take into account the internal stresses existing in solidified systems.⁵³

High stability is characteristic of nanoparticles prepared *in situ* by combining photopolymerisation (acrylamide and *N,N'*-methylene-bis-acrylamide, non-filtered light from a DRSh-250 mercury lamp), and photoreduction of highly stable Ag^+ ions.⁷⁶ In the presence of atmospheric oxygen, the nascent specimens remain stable for a few weeks, and films formed remain unaltered for a few months. The size of Ag particles (≤ 20 nm) is comparable with that of nanoparticles prepared by the method of combined low-temperature condensation of vaporised metals. A modification of this method was reported recently.¹⁹¹ It consists in the combined condensation, on a support refrigerated with liquid nitrogen, of the vapour of metals (Ag, Pb, Cd, or Mg) and monomers capable of low-temperature polymerisation (specifically, *n*-xylylene), which yields poly-*n*-xylylene films with regularly distributed nanoparticles more or less homogeneous in size. The formation of these films was induced by UV irradiation at 80 K or heating to 130–160 K.

Other modifications of this method for the preparation of nanoparticles in polymers have also been reported. Let us note here only one of them, in which the catalysts containing highly dispersed particles of transition metals immobilised in polymeric films were obtained by the electrolytic oxidative polymerisation of a monomer derived from mercaptohydroquinone containing metals of platinum group incorporated by electrochemical deposition.¹⁹²

Not all of the approaches considered in this section are equally developed. The priority is given to the reduction techniques. The role of the dispersive phase is mostly played by carbon-chain polymers and less often, by condensation-type polymers. The immobilisation of nanoparticles is nearly always accompanied by interaction of the particles formed with the matrix, in contrast to mechanical mixtures of metals with polymers.

V. Polymer-analogous transformations in the immobilisation of metal clusters

Although the polymer-immobilised systems considered above are characterised, as a rule, by high dispersity, by homogeneous distribution of nanoparticles over the polymer bulk, and sometimes by the irreversible sorption of macromolecules on the surface of colloidal particles, which remain in the gel state over a

Table 3. IR and PMR spectra of molecular and polymer-immobilised carbonyl clusters.

Cluster	IR Spectra ($\nu_{C=O}$ / cm^{-1})	PMR Spectra (δ /ppm)	Ref.
$\text{Ir}_4(\text{CO})_{11}\text{PPh}_3^a$	2088, 2056, 2020, 1887, 1847, 1825		206
$\text{P}-\text{PPh}_2\text{Ir}_4(\text{CO})_{11}$ (membrane)	2087, 2055, 2017, 1848		206
$\text{Ir}_4(\text{CO})_{10}\text{Diop}^a$	2070, 2040, 2011, 1986, 1870, 1833, 1791		206
$\text{P}-\text{Diop}[\text{Ir}_4(\text{CO})_{11}]_2$ (membrane)	2088, 2057, 2020, 1845		206
$\text{P}-\text{Diop}[\text{Ir}_4(\text{CO})_{10}]$ $\text{P}-\text{Diop}[\text{Ir}_4(\text{CO})_{11}]_2$ (membrane)	2068, 2040, 2012, 1991, 2088, 2054, 2021		207
$\text{Os}_3(\text{CO})_{10}\text{Cl}_2^b$	2116, 2081, 2069 2027, 2015, 1993, 1989		207
$\text{Os}_3(\text{CO})_8\text{Cl}_2(\text{PPh}_3)_2^b$	2079, 2014, 2004, 1967, 1943		207
$\text{P}-\text{PPh}_2)_2\text{Os}_3(\text{CO})_8\text{Cl}_2$ (block-copolymer)	2096, 2073, 2036, 2007, 1997, 1959, 1939		207
$\text{P}-\text{PPh}_2\text{Os}_3(\text{CO})_{10}\text{Cl}_2$ (statistical copolymer)	2096, 2073, 2060, 2029, 2007, 1994, 1955, 1940		207
$(\text{PPh}_3\text{Cu}-\mu_3)\text{FeCo}_3(\text{CO})_{12}$	2074, 2012, 1978, 1972, 1850		208
$\text{P}-\text{PPh}_2-\text{Cu}-\mu_3\text{FeCo}_3(\text{CO})_{12}$	2065, 2000, 1969, 1956, 1840		208
$(\text{PPh}_3\text{Au}-\mu_3)\text{FeCo}_3(\text{CO})_{12}$	2075, 2003, 1969, 1930, 1823		208
$\text{P}-\text{PPh}_2-\text{Au}-\mu_3\text{FeCo}_3(\text{CO})_{12}$	2066, 1993, 1960, 1930, 1813		208
$(\mu\text{-H})\text{Os}_3(\mu\text{-4-VPy})(\text{CO})_{10}^c$	2101, 2061, 2051, 2020, 2008, 2000, 1988, 1973	8.01, 7.25, 6.25, 5.72, — 14.85 [$\text{Os}_2(\mu\text{-H})$]	209
$(\mu\text{-H})\text{Os}_3(\mu\text{-4-VPy})(\text{PPh}_3)(\text{CO})_9^{\text{d,e}}$	2087, 2047, 2012, 2004, 1997, 1984, 1975, 1945	7.32, 6.51, — 5.71, — 14.13 [$\text{Os}_2(\mu\text{-H})$]	209
$\text{Os}_3\text{H}(\text{CO})_5\text{Py}^c$	1940, 2040,	10.5, 12.0 13.75	210
$(\mu\text{-H})\text{Ru}_3(\mu\text{-SCH}_2\text{CH}=\text{CH}_2)(\text{CO})_{10}^{\text{c,d}}$	2108, 2069, 2059, 2022, 2020, 2000, 1988, 1955 (ν_{CO}), 1636 ($\nu_{C=C}$)	5.87, 5.28, 2.82, — 15.38 ($\text{Ru}_2(\mu\text{-H})$)	209
$\text{Rh}_6(\text{CO})_{15}(4\text{-VPy})_2^{\text{c,f}}$	2104, 2068, 2038, 2010, 1788 (ν_{CO}), 1619 ($\nu_{C=C}$)	7.39, 8.88, 6.68, 6.10, 5.68	211
$\text{Rh}_6(\text{CO})_{14}(4\text{-VPy})_2^{\text{c,f}}$	2090, 2056, 2028, 1760 (ν_{CO}), 1619 ($\nu_{C=C}$)	7.35, 8.81, 6.65, 6.06, 5.63	211
$\text{P}-\text{PPh}_2\text{Fe}(\text{CO})_4$	2060, 1975, 1940, 1897, 1875		212
$\text{Fe}(\text{CO})_4\text{PPh}_3$	1875		

^a Diop is 2,3-isopropylidenedioxy-1,4-bis(diphenylphosphino)butane moieties; IR spectrum in CH_2Cl_2 ; ^b IR spectrum in cyclohexanone; ^c ^1H NMR spectrum in CDCl_3 ; ^d IR spectrum in hexane; ^e ^1H NMR spectrum in CD_2Cl_2 . ^f IR spectrum in chloroform.

The features of polymer-immobilised clusters formation may be reduced in the most general form to the following statements.^{213–218} If the concentration of phosphine groups in the macroligand is low (*i.e.*, less than 2% of benzene rings are phosphorylated, see Scheme 8) or the PPh_2 groups are randomly distributed, then polymer-immobilised clusters are formed in which the metal cluster, particularly, of Ir, is bound with one PPh_2 group of the polymer. In the case of higher concentration of PPh_2 groups (with over 3% of functionalised benzene rings), a mixture of clusters is formed that are bound with one or two groups of the polymer. The product with two bonds is virtually the only one formed in the case of the styrene–divinylbenzene–vinylidiphenylphosphine block copolymer containing 8%–15% of PPh_2 groups.

The ligand exchange of the functional groups carrying equivalent numbers of electrons is a typical mode of immobilisation of clusters that undergo fast dissociation, which is especially characteristic of clusters of the $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ type. The exchange between the phosphine ligands of clusters and the phosphorus-containing groups in the polymer occurs under milder conditions than that involving the carbonyl ligands. Thus, an attempt to bind the carbonyl $\text{Ir}_4(\text{CO})_{12}$ with a phosphorus-containing polymer has failed. Therefore, use is commonly made of mixed phosphine- and carbonyl-containing clusters as the precursors of polymer-immobilised nanoparticles (see Scheme 9).

In some cases, the immobilisation process leads to the appearance of small aggregates with indefinite structure. These polymer-bound particles can in principle be carbonylated or decarbonylated with the formation of clusters of definite structure. The

reaction conditions markedly affect the binding of clusters and the polymers. When $\text{Rh}_4(\text{CO})_{12}$ reacts with P-PPh_2 in hexane at 50°C , binuclear clusters are formed.²¹⁶ When this reaction is carried out in benzene containing $\text{Rh}_6(\text{CO})_{16}$, the reactor walls become covered with black spots of deposited atomic rhodium $2.5\text{--}4.0\text{ nm}$ in diameter (*i.e.*, about 100 Rh atoms in each spot).²¹⁷ The decrease in the reaction temperature and the use of CO lead to the immobilisation of $\text{Rh}_6(\text{CO})_{13}(\text{PPh}_3)_3$ clusters. The increase in the temperature affects noticeably the behaviour of immobilised Ru clusters: they dissociate at $100\text{--}150^\circ\text{C}$ to form crystalline ruthenium. Interestingly, the cluster anion $\text{Ru}_5\text{Cl}_7^{2-}$ cannot penetrate inside the polymeric matrix for steric reasons, and an attempted binding to the PPh_2 group resulted in the dissociation of this anion with eventual formation of immobilised mono- and bi-nuclear complexes. Along with the immobilisation, decarbonylation may occur, which is particularly characteristic of the Fe and Co clusters, apparently because of similar energies of M-M and M-CO bonds (about 113 kJ mol^{-1}). The addition of $\text{Fe}_3(\text{CO})_{12}$ to P-PPh_2 leads to the fragmentation and formation of a monosubstituted complex $\text{P-PPh}_2\text{Fe}(\text{CO})_4$ and traces of $\text{P-(PPh}_2)_2\text{Fe}(\text{CO})_3$.¹⁹⁵ It is noteworthy that the homogeneous reaction of $\text{Fe}_3(\text{CO})_{12}$ with the excess of PPh_3 yields nearly equal quantities of mono- and di-substituted products. Thus, the polymeric ligand brings about definite steric control. Subsequent thermal or photochemical impacts result in the decomposition of mononuclear carbonyl complexes with the formation of 'ligand-free' clusters dispersed in the polymer.

Of other phosphorus-containing polymers used for the immobilisation purposes, the most interesting seems to be the macro-ligand modified by optically active groups of 2,3-isopropylenedioxy-1,4-bis(diphenylphosphino)butane on which the cluster fragments of $\text{Ir}_4(\text{CO})_{12}$ may be immobilised.²¹⁹

The distribution of functional groups and clusters that are formed over the bulk of the polymer is of principal significance, since the homogeneity of dispersion is a sign of the isotropy of the polymeric material. In this context, scanning electron microscopy was used to study the distribution of P and Pd along the diameter of the spherical granules of immobilised three-nuclear Pd clusters (Fig. 6).²²⁰ The immobilisation may be performed in such a way so as to allow either uniform distribution of metal clusters along the diameter of the granule (2% of cross-links) or their preferential localisation in a thin subsuperficial layer (20% of cross-links) 0.2 mm thick, the diameter of the granule being 1 mm . The phosphorus-containing groups are distributed uniformly over the entire thickness of granules. The structure of the polymer-

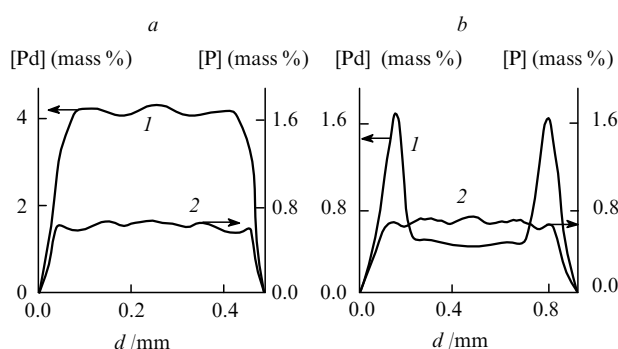
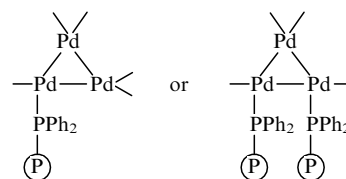
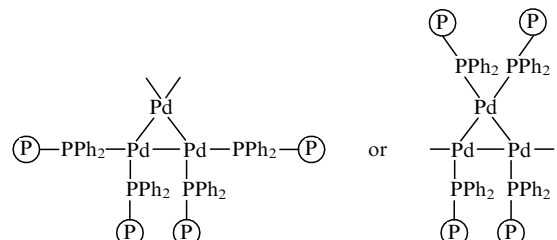


Figure 6. Distribution of palladium (1) and phosphorus (2) as a function of granule diameter in the palladium-immobilised phosphorylated polystyrene with the cross-linking degree of 2% (a) and 20% (b).

immobilised clusters depends on the $[\text{P}]:[\text{Pd}]$ ratio. In the case of polymers with 2% of cross-links and $[\text{P}]:[\text{Pd}] < 1$, the structure may be schematically presented in the following form:



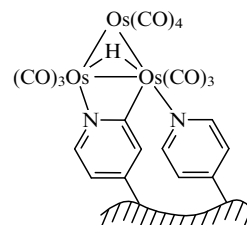
However, one can hardly imagine, at least for steric reasons, the structures that would be formed at $[\text{P}]:[\text{Pd}] > 1$:



Data on the immobilisation of clusters by polymers with other functional groups, *e.g.*, nitrogen-containing (aminated PS, P4-VPy, amino-containing ion-exchange resins of Amberlyst A-21 type, *etc.*) are more scarce. Carbonyls $\text{Rh}_6(\text{CO})_{16}$, $\text{Rh}_4(\text{CO})_{12}$, and $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ interact with aminated PS resulting in $\text{P-CH}_2\text{NMe}_2\text{HRh}_x(\text{CO})_y$ compounds.²²¹ The product of the Os_3 cluster binding by this ligand has the composition $\text{HOs}_3(\text{CO})_{11}\text{N}^+\text{Et}_2\text{CH}_2\text{CH}_2\text{-P}$.²²² Similarly $\text{Ru}_3(\text{CO})_{12}$ is bound to macroporous chelating polymers functionalised with dipyriddy, 2-aminopropyl, 2-aminophenyl, and other groups. An anionic trinuclear iron cluster is immobilised through the NR_4^+ group on a $10\text{ }\mu\text{m}$ -thick ion-exchange membrane. $[\text{Pt}_{15}(\text{CO})_{30}]^{2-}$ cluster is bound by the hydrophilic polymer QAE-Sephadex containing diethyl(2-hydroxypropyl)aminoethyl groups.²²³

The interaction of metal clusters with the amino-containing macroligands, contrary to that with the phosphorus-containing macroligands, yields a large number of by-products, especially when the polymer carries the primary and secondary amino groups. For example, the reactions involving carbonyl clusters of ruthenium and osmium lead to the activation of α - and β -C-H bonds, *trans*-alkylation (at $25\text{--}45^\circ\text{C}$), and even the cleavage of C-N bonds (at $125\text{--}143^\circ\text{C}$). The latter refers also to the interaction of tertiary amines with Os_3 clusters.

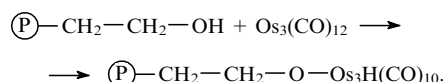
The mechanism underlying the binding of $\text{Rh}_4(\text{CO})_{12}$ clusters by the 4-VPy macromolecules is not completely clear. The interaction of $\text{Os}_3(\text{CO})_{12}$ with 4-VPy is carried out in DMF under CO for 3 h at 110°C .²¹⁰ The structure of the product is difficult to interpret: the IR spectrum reveals two intense absorption bands with maxima at 2040 and 1940 cm^{-1} . These data in combination with those from ^1H NMR (Table 3) allowed an inference that the cluster fixation involves two pyridine rings of the polymer of which one is chelating. This mode of binding becomes possible owing to the flexibility of the polymeric chain.



Note also that the preservation of the polynuclear structure or its disintegration depend also on the nature of the proper ligand groups of the cluster. As a rule, the contribution to the cluster energetics from the ligand environment is rather large and diminishes as the nuclearity increases.²¹ In the binding of the acetate complex $[\text{Rh}_2(\text{OCOCH}_3)_4]$ by polymers containing 3(5)-methylpyrazole or imidazole groups,²²⁴ the binuclear structure is preserved and the rhodium retains its oxidation state $2+$, whereas

in its binuclear complexes with acetonitrile, sulfate, and hexafluoroacetylacetonate the cleavage of the Rh–Rh bond occurs with the increase in Rh oxidation state. Thus, the cleavage of the Rh–Rh bond is favoured by the labile ligands which can be substituted by the amino groups, while in the case of binuclear Rh^{2+} complex the contracting action of bridging acetate groups favours the preservation of the initial structure.

The O- and S-containing matrices, including polymeric alcohols and ketones, are less often used for the immobilisation of clusters. The binding of an Os_3 cluster to polymeric alcohols follows, as in the case of inorganic oxides, the mechanism of oxidative addition:²²⁵



High stability is characteristic of di- and tri-nuclear Ru complexes of the type $\text{Ru}^{3+}-\text{O}-\text{Ru}^{4+}-\text{O}-\text{Ru}^{3+}$, that are readily bound by the ion-exchange resin CR-10 containing iminodiacetate groups.²²⁶

Metal clusters can also be immobilised on natural cyclodextrins.²²⁷ The cavity of γ -cyclodextrin, in contrast to that α - and β -cyclodextrins, is large enough to accommodate not only metal ions but also bi-, tri-, and even tetra-nuclear clusters (Fig. 7). It is significant that the incorporation of clusters into the γ -cyclodextrin cavities increases considerably their stability. For instance, the tetranuclear Co cluster dissociates at 393 K, whereas the product of its interaction with γ -cyclodextrin disintegrates only above 473 K.

Formally polynuclear formations, such as 12-heteropolyacid of Keggin type $\text{H}_n[\text{XM}_{12}\text{O}_{40}]$, where X stands for heteroatom and $\text{M} = \text{Mo}$ or W , can also be immobilised on polymers. When they are stirred with 4-VPy at 30–35 °C, a product is formed in which,

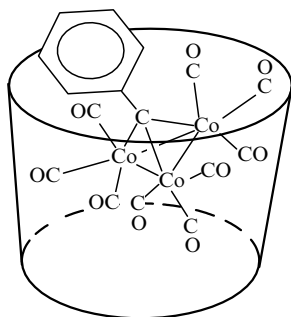


Figure 7. Supposed structure of an inclusion compound formed by a cluster complex of Co and γ -cyclodextrin.

according to IR spectroscopy and chemical analysis data, one $\text{H}_4[\text{SiMo}_{12}\text{O}_{40}] \cdot 13\text{H}_2\text{O}$ molecule binds four protonated vinylpyridine units, and $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$ binds three such units.²²⁸ The repeating units in the structures formed have the formulae $(\text{H}_4\text{-VPy})_4[\text{SiMo}_{12}\text{O}_{40}]$ and $(\text{H}_4\text{-VPy})_3[\text{PMo}_{12}\text{O}_{40}]$. The same type of binding is observed in the immobilisation of 12-heteropoly acids on water-soluble polyelectrolytes, viz., alkylated poly-(2-methylvinylpyridine), and poly(dimethyldiallylammonium) chloride:²²⁰ the negative charge of the heteropolyanion is compensated by positive charges of the polymeric chain.

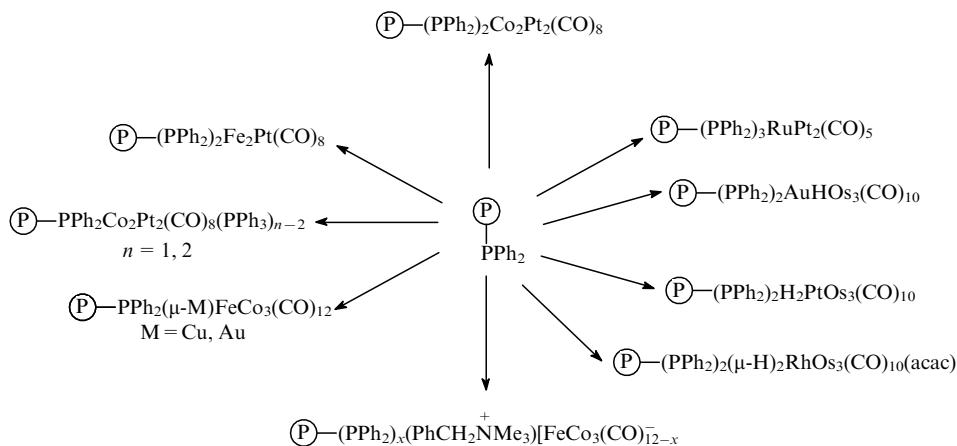
2. Polymer-immobilised heteropolymetallic compounds

It is known that the heterometallic polynuclear centre is preferred to the monometallic one in the solution of numerous problems, in particular, in the field of catalysis. Immobilised particles of this type may be regarded as models of bimetallic catalysts that find industrial use for the reforming of petroleum fractions. However, in contrast to the industrial alloy-based catalysts, the bimetallic clusters are structurally homogeneous.

The binding of heterometallic clusters and the identification of the products may be based, as a rule, on much the same approaches as those used for the immobilisation of monometallic clusters. Usually, they are assembled from monometallic complexes or clusters (for example, through the joint decomposition of $\text{H}_2\text{PtCl}_6 - \text{Fe}(\text{NO}_3)_2$ or $\text{Rh}_4(\text{CO})_{12} - \text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ mixtures in polymers). There are strong grounds for stating that bimetallic clusters are formed in colloidal dispersions of Pt and Pd stabilised by PVPr^{159–161} at the initial molar ratio $[\text{Pd}]:[\text{Pt}] = 4:1$. In some instances, the preparation of required products is based not on the monomeric clusters but rather on the cluster compounds with different metals. Thus ion-exchange resins were brought into reaction with mixtures of $\text{Rh}_4(\text{CO})_{12}$ and $\text{Co}_4(\text{CO})_{12}$ in the molar ratio from 3:1 to 1:1.²¹⁹

In the immobilisation, the preference is given to the heterometallic clusters with identified structures.[‡] In most cases, the matrix is formed by $\textcircled{\text{P}}-\text{PPh}_2$, and the immobilisation is performed by means of ligand or ion exchange. A reliable technique for the identification of the structure of the polymer-bound products is comparison of the IR spectra of their carbonyl groups

[‡] The number of known compounds in which one molecule contains several metal species exceeds 100. The common principle of their synthesis consists in the substitution of one metal by another in high-symmetry metallopolyhedrons with the preservation of the total number of cluster valent electrons and the type of ligands. The most common are the heterodi-, heterotri-, and heterotetra-metallic clusters obtained by addition, substitution, elimination, and restructuring. Their stability is enhanced by centring with μ_3 -bridges consisting of elements of the main subgroups (specifically, C, S, P). The common aspects of the synthesis of these compounds, their structure, and classification based on the topology–geometry principle have been reviewed.²²⁹



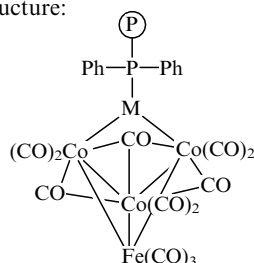
Scheme 10

with the spectra of low-molecular-weight models. Typical examples of the immobilisation of intact heterometallic clusters on P-PPh_2 are shown in Scheme 10.^{3, 207, 214, 230, 231}

Also worthy of note is the binding of $\text{H}_2\text{FeOs}_3(\text{CO})_{13}$ by cross-linked macroporous chelating polymers.²³² There are reports of the immobilisation of $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$ on Dowex-1 ion-exchange resin,²³³ as well as of $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$, $[\text{FeRh}_4(\text{CO})_{15}](\text{NMe}_4)_2$, and $\text{Rh}_{4-x}\text{Co}_x(\text{CO})_{12}$ ($x = 2, 3$) on different macroligands. The mechanisms of these reactions remain obscure.

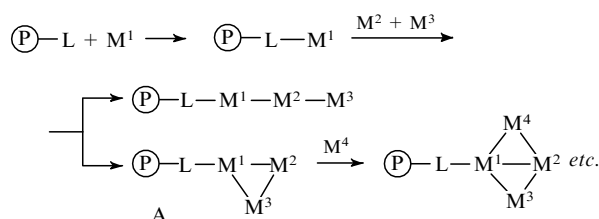
The binding of bimetallic Keggin heteropolyacids, *e.g.*, $\text{H}_6[\text{CoW}_{12}\text{O}_{40}]$,²²⁸ to P4-VPy is analogous to that of monometallic ones. The repeating units have the composition $(\text{H}_4\text{-VPy})_4\text{H}_2[\text{CoW}_{12}\text{O}_{40}]$. In principle, similar processes can occur with polyoxoanions of niobium-containing polytungstates, such as $[(\text{CO})_2\text{Rh}]_5[\text{Nb}_2\text{W}_4\text{O}_{19}]_2^{3-}$, $[(\text{CO})_2\text{Ir}]_2\text{H}[\text{Nb}_2\text{W}_4\text{O}_{19}]_2^{5-}$ and others.²³⁴

The compounds mentioned above are formally of the trimetallic type. The trimetallic clusters bound with P-PPh_2 are obtained by the assembly method, *i.e.*, through the interaction of a polymer with MPPH_3Cl ($\text{M} = \text{Cu}$ or Au) and subsequent treatment of the product with the tetranuclear bimetallic cluster $\text{FeCo}_3(\text{CO})_{12}$.²⁰⁸ The cluster thus obtained has the following structure:



The general strategy for the preparation of heterometallic clusters possessing high nuclearity may be described by Scheme 11.

Scheme 11



Most probably, the reaction involves the formation of heterometallic rings. The trimetallic units of type A serve as building blocks in the chemistry of clusters.²³⁵

The polymer-immobilised clusters of polymetallic type are more stable than the initial ones: the decomposition temperature of the cluster $(\text{PPh}_3)\text{CuFeCo}_3(\text{CO})_{12}$ is 170–178 °C, while its polymeric analogue dissociates at 186–193 °C. The clusters based on gold are always less stable than the copper-containing ones (the dissociation temperatures of the initial and fixed gold clusters are 163–165 and 171–176 °C, respectively). In general, the immobilisation increases the thermal stability of both the cluster and the binding polymer. Heterometallic clusters are also often immobilised on the surface of inorganic polymers. For instance, worthy of note is the fixation of $[\text{Fe}_6\text{C}(\text{CO})_{16}](\text{Et}_4\text{N})_2\text{HFeCo}_3(\text{CO})_{12}$, $[\text{Rh}_5\text{Fe}(\text{CO})_{16}](\text{Et}_4\text{N})$, $[\text{RhFe}_5\text{C}(\text{CO})_{16}](\text{Et}_4\text{N})$ and other clusters on SiO_2 .²³⁶ According to the data from IR spectroscopy, the clusters do not undergo any changes in this case, except for the cluster based on RhFe_5 that reacts vigorously with SiO_2 . The attempts to bind the clusters $\text{H}_2\text{FeRu}_3(\text{CO})_3$ and $\text{Fe}_2\text{Pt}(\text{CO})_8(\text{PPh}_3)$ with phosphorylated silica gel were unsuccessful.²³¹ A number of bimetallic clusters were encapsulated in channels of zeolites, while the clusters $\text{Rh}_{4-x}\text{Co}_x(\text{CO})_{12}$ ($x = 2, 3$) were immobilised by deposition on carbon.^{237–239}

The method of ‘layering’ was used for the binding of Prussian blue and its analogues with polyvinylamine hydrochloride: salts of the type MCl_2 ($\text{M} = \text{Fe}, \text{Co},$ and Cu) bound with ions $[\text{Fe}(\text{CN})_6]^{n-}$ ($n = 3$ or 4) were fixed on a polymer in aqueous solutions.²⁴⁰ The logarithms of the formation constants of binuclear complexes from mononuclear immobilised complexes of Fe, Co, and Cu are 9.8, 7.7, and 10.4 in litre mol^{-1} units, respectively. Although the degrees of freedom of the polymeric chain and the cluster decrease upon formation of polynuclear complexes, the ΔS value remains positive, which is indicative of the entropy increase, apparently due to the release of several molecules of water bound initially to M^{2+} and $[\text{Fe}(\text{CN})_6]^{n-}$.

One can conclude that the studies on the immobilisation of heterometallic clusters are making rapid progress, although this research area has still numerous problems related mainly to the mechanism underlying the interaction of clusters and functional groups of polymers, transformations of immobilised reactants, and the structure of final products.

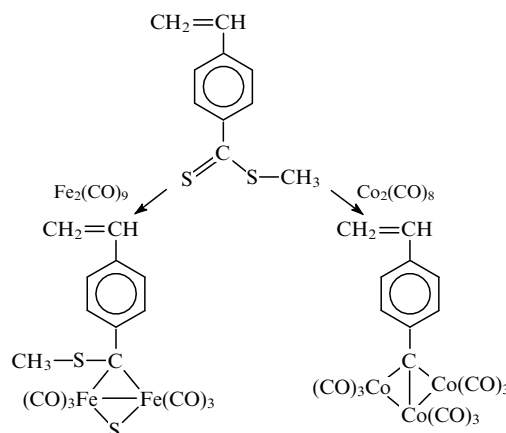
3. Polymerisation and copolymerisation of cluster-containing monomers as a route to the production of polymer-immobilised metaloclusters

By analogy with the formation of nanoparticles by means of polymerisation of appropriate monomeric mixtures (simultaneous formation of the matrix and nanoparticles, see Section IV), it could be expected that the polymerisation and copolymerisation of cluster-containing monomers are very simple one-step methods for the preparation of cluster-containing polymers. It was presumed that the major problem would be the synthesis of the appropriate monomers.

Recently, two promising approaches have been developed for the synthesis of cluster-containing monomers.^{241, 242} According to the first approach, the groups capable of polymerisation are introduced as ligands into the known clusters. To this end, recourse is made to the replacement of the intrinsic ligands of clusters by their analogues carrying multiple bonds, oxidative binding, addition of new groups on multiple $\text{M}-\text{M}$ bonds under mild conditions, *etc.* These reactions may lead to a higher or lower nuclearity of clusters. The reaction of $\text{Ru}_3(\text{CO})_{12}$ with dimethyl fumarate in boiling heptane results in the formation of complexes with different nuclearity, their relative yields being dependent on the ratio of reagents and the duration of the reaction.²⁴³

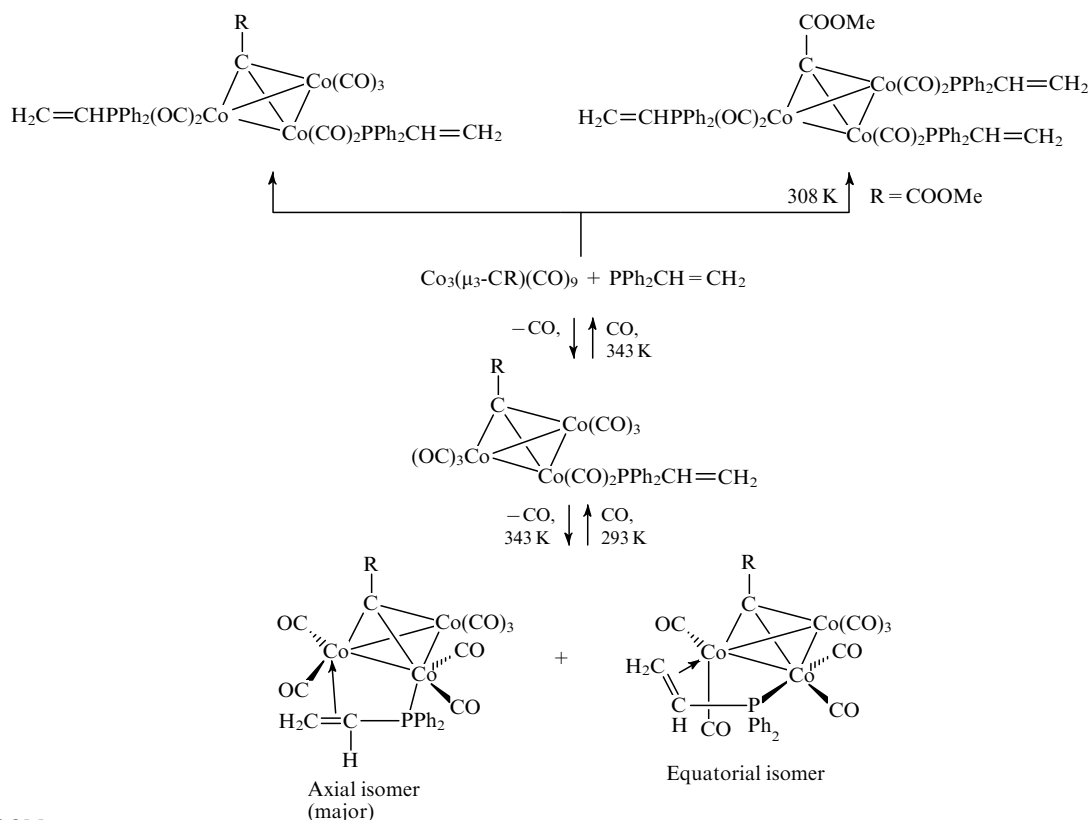
The second approach consisting in the build-up of conventional monomers with clusters is not as popular as the former. A characteristic example of this approach is the preparation of cluster monomers based on methyl *p*-vinylthiobenzoate (Scheme 12).^{244, 245}

Scheme 12



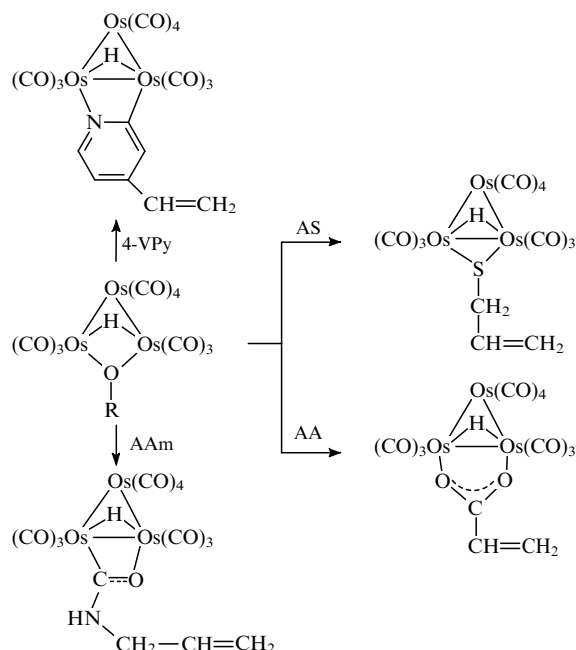
Although these reactions are complicated by a number of side processes (desulfurisation, formation of metal sulfides and products of ortho-metallation, *etc.*) not allowing the achievement of yields of target products above 40%, it is essential that the cluster skeletons are preserved, and the monomers formed can undergo polymerisation.

Scheme 13

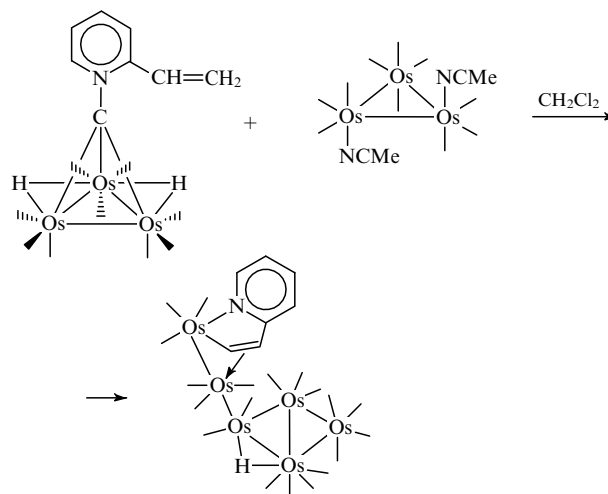


An example of a more convenient route to the synthesis of this class of potential monomers is the reaction of tricobaltalkylidene complexes $\text{Co}_3(\mu_3\text{-CR})(\text{CO})_9$ with vinylphosphine ligands in heptane at 308 K. This allowed the isolation and characterisation of $\text{Co}_3(\mu_3\text{-CR})(\text{CO})_{9-x}(\text{PPh}_2\text{CH}=\text{CH}_2)_x$ ($x = 1, 2, 3$).²⁴⁶ When the product with $x = 1$ is heated to 343 K, it eliminates CO groups (Scheme 13), and an additional coordination of vinyl groups with Co atom occurs.

High yields of cluster-containing monomers were obtained from trinuclear clusters $\text{M}_3(\text{CO})_{12}$ ($\text{M} = \text{Os}, \text{Ru}$), $\text{Os}_3(\text{CO})_{11}(\text{-MeCN})$, $\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2$, and $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}$. $(\mu\text{-OR})$ ($\text{R} = \text{H}, \text{Rh}$), and conventional monomers (4-VPy, acrylic acid (AA), allylamine (AAM), allyl sulfide (AS), *etc.*):²⁰⁹



Interestingly, like in the above-considered system obtained by the immobilisation of $\text{Os}_3(\text{CO})_{12}$ on P-4-VPy , the pyridine ring in the monomer based on 4-VPy was chelated. The complex $\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2$ reacts rapidly with 2VPy to form a trinuclear cluster $\text{HOs}_3(\text{CO})_9\text{L}(2\text{VPy})$ ($\text{L} = \text{CO}$ or PMe_2Ph). The preparation of a triosmium alkylidene cluster $\text{H}_2\text{Os}_3(\text{CO})_9[\mu_3\text{-(2VPy)}]$, which may be used as the starting material for the preparation of planar hexaosmium carbonyl cluster with an open structure, has been described.²⁴⁷



The reaction of 4-VPy with $\text{Rh}_6(\text{CO})_{16}$ in the presence of acetonitrile or trimethylamine *N*-oxide occurs under mild conditions and yields a monosubstituted derivative $\text{Rh}_6(\text{CO})_{15}(4\text{-VPy})$ as the major product and a small amount of $\text{Rh}_6(\text{CO})_{14}(4\text{-VPy})_2$, which can be easily isolated in a pure state by chromatography.²¹¹ Contrary to the osmium derivative, the monomer $\text{Rh}_6(\text{CO})_{15}(4\text{-VPy})$ is an octahedral cluster with 11 terminal and 4 μ_3 -bridging carbonyl ligands, and the vinylpyridine moiety is linked with the rhodium atom only through the nitrogen atom and

occupies the coordination position of the twelfth terminal CO. The mean length of the Rh–Rh bond is 0.2762 nm, which is close to that in other Rh clusters. Apparently, this mechanism also operates in the reaction of Rh clusters with the allylic ligand $\text{Ph}_2\text{PCHCH}=\text{CH}_2$.²⁴⁸

The metallomonomers considered above incorporate only carbonyl clusters, though the solution of numerous problems requires monomers and polymers that contain other type of clusters, *e.g.*, halogenated ones.

Mo(II) halides, which readily form polynuclear complexes (of $\text{Mo}_6\text{Cl}_{12}$ type) owing to a strong trend of divalent molybdenum to association, are highly promising.²⁴⁹ Of special interest are the complexes with a stable group $[\text{Mo}_6\text{Cl}_8]^{4+}$, which is named a staphylonuclear group (Fig. 8). This group includes an octahedron with six molybdenum atoms surrounded by eight chlorine atoms localised in the apices of a slightly distorted cube. The octahedron is inscribed into the cube so that the Mo(II) atoms are localised at the centres of facets. It is this circumstance that provides for the existence of six equivalent directions (normals) along which the effect of shielding of molybdenum atoms by chlorine atoms is minimal. The diameter of this cluster may be estimated at ~ 1 nm (as the sum of a cube diagonal Cl–Cl equal to 0.6 nm and the radii of two chlorine atoms, each being 0.18 nm). The stable staphylogroup plays the crucial role in the complexation reactions.^{250, 251} It can bind up to six axial ligands, negative ions or polar molecules, including those containing multiple bonds thus making possible polymerisation of monomers. For the first time, vinylimidazole and vinylpyrrolidone were used as ligands.^{252, 253} In principle, conventional vinylic monomers, *e.g.*, 4-VPy, acrylonitrile, acrylamide, *etc.*, can serve as these ligands.²⁵⁴

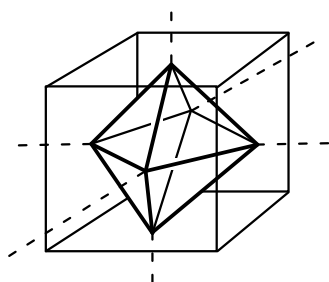
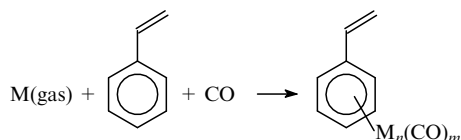


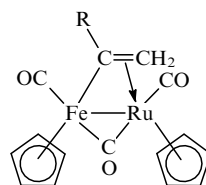
Figure 8. Structure of the staphylonuclear group $[\text{Mo}_6\text{Cl}_8]^{4+}$.

The methods of the synthesis and polymerisation of cluster-containing monomers are still in their infancy, though a breakthrough in this direction may be expected in the near future. For example, there are no essential restrictions on the application of the above-considered method of vaporisation of atomic metals to this end (see Section IV).



Recently, cryosynthesis involving atomic chromium and phenylacetylene as reagents has yielded Cr-containing polymeric products along with cyclotrimers of phenylacetylene.²⁵⁵ The condensation of vapour of gold with large excess of a diacetylene monomer has been recently accomplished.⁶⁷

These methods apply equally to the creation of monomers based on heteropolynuclear clusters. One possible way consists in the introduction of groups with multiple bonds into heterometallic complexes. For example, treatment of the iron–ruthenium complex $[\text{FeRu}(\text{CO})_4(\eta^5\text{-C}_5\text{H}_5)_2]$ with olefins yields μ -vinylic complexes ($\text{R} = \text{H}, \text{Ph}$) with Fe–Ru bonds.²⁵⁶



In these complexes, the atoms of Fe and Ru are linked with alkenes through the σ - and π -bonds, respectively. The reactivity of bimetallic complexes as regards transformations of unsaturated hydrocarbons is close to that of homonuclear ones and decreases in the series $\text{FeRu} > \text{Fe}_2 > \text{Ru}_2$. The group of potential heterometallic monomers may be extended to include $\text{FeCo}(\text{CO})_7$, $(\mu\text{-CH}=\text{CHR})$,²⁵⁷ bimetallic η^2 -complexes of Mo, V, or Fe with formaldehyde bridging,²⁵⁸ and a number of other compounds (for example, AuPt_2 -based clusters).²⁵⁹ The acetylenide cluster of Pt_2Cu_4 (**2**) was prepared by treatment of 1,1'-[chloro(η^4 -cyclooctadiene)platino]ferrocene (**1**) with an excess of phenylacetylene and CuI (Scheme 14). The same product is obtained from [phenylethynyl(η^4 -cyclooctadiene)platino]ferrocene (**5**). The bis-substituted ferrocene **3** gives the cluster **4** (Scheme 14, Fig. 9). The Pt–Cu bond length is 0.2845–0.2975 nm.

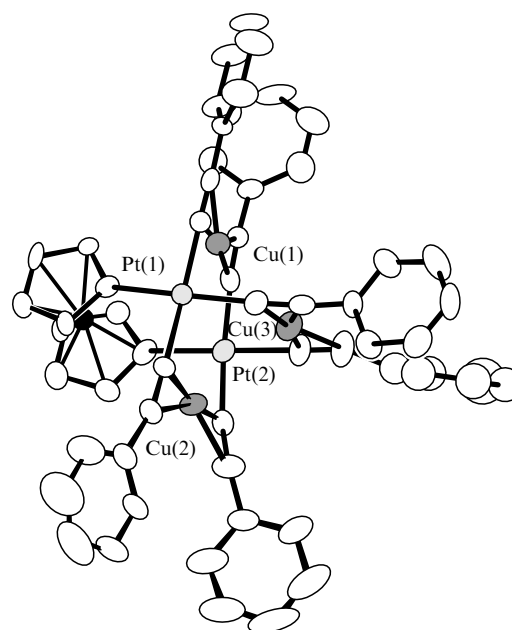
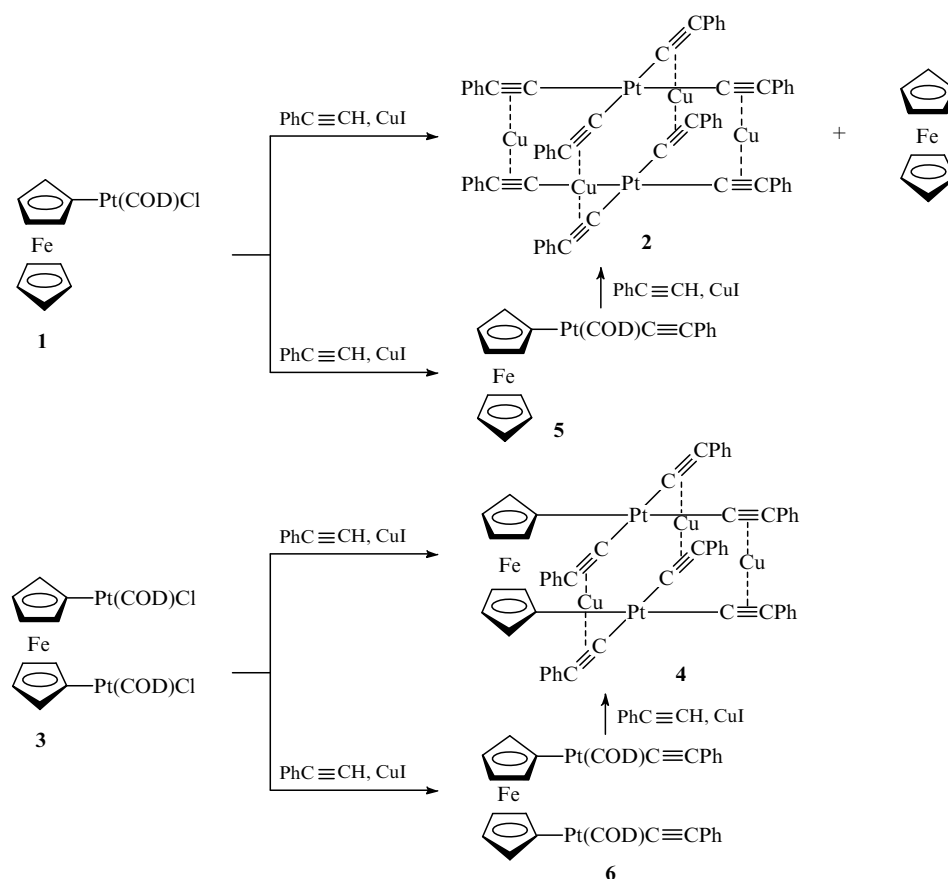


Figure 9. Molecular structure of the complex **4** (the hydrogen atoms are not shown).

One may also consider the monomers comprising atoms of the same metal in different valent states, *e.g.*, FeCl_2 , $(\text{FeCl}_3)_2(\text{CH}_2=\text{CHCN})_6$, as heterometallic ones.²⁶¹

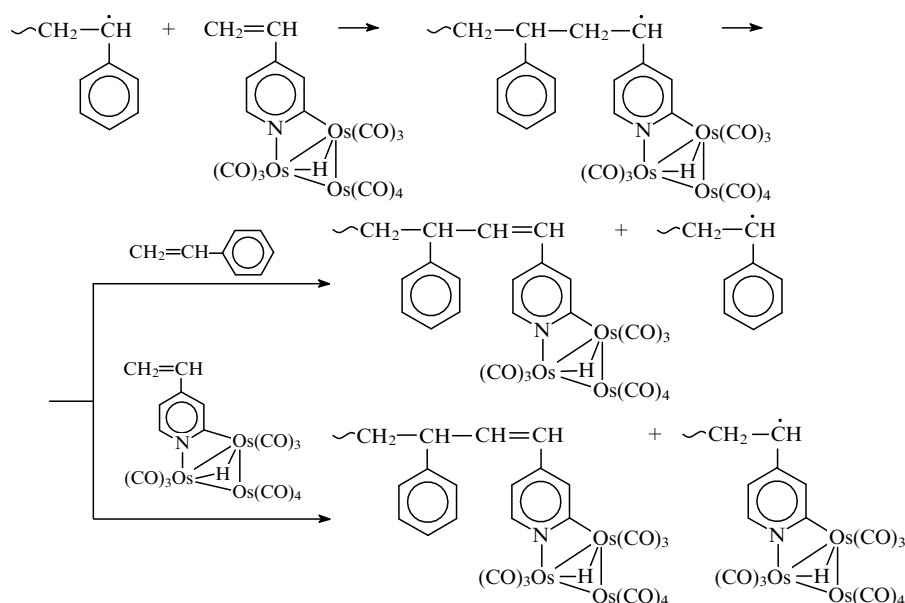
Numerous attempts to polymerise cluster monomers²⁶² have always faced insurmountable problems associated with the presence of such bulky substituents as cluster fragments possessing specific electronic structures, with the reaction of the initiating radicals or ions with cluster-containing monomers leading to their degradation, *etc.* These complications rule virtually out the possibility of homopolymerisation of these exotic metallomonomers. The most successful proved to be the attempt to copolymerise monomers derived from dicobalt octacarbonyl or diiron nonacarbonyl and dithioesters (Scheme 12) or thioamides with styrene or *N*-[tris(hydroxymethyl)methyl]acrylamide. This copolymerisation has led to the products containing up to 1 mol.%–2 mol.% of units with intact cluster framework (Table 4). The copolymers produced possessed large molecular weights.

Scheme 14



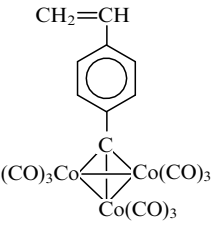
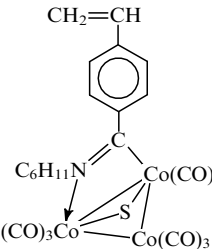
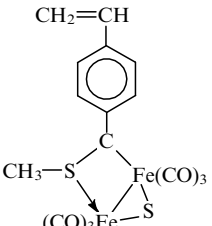
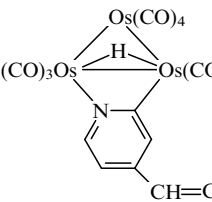
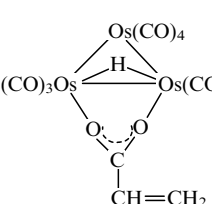
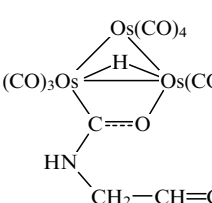
Special studies on styrene polymerisation in the presence of $\text{Os}_3(\text{CO})_{12}$ and $(\mu\text{-H})\text{Os}_3(\mu\text{-4-VPy})(\text{CO})_{10}$ have shown²⁶³ that the starting cluster $\text{Os}_3(\text{CO})_{12}$ has no influence on either the rates of the initiator degradation and styrene polymerisation or the molecular-weight parameters of the PS produced. The homopolymerisation of $(\mu\text{-H})\text{Os}_3(\mu\text{-4-VPy})(\text{CO})_{10}$ proceeded with difficulty: an oligomer with 5–6 units in the chain was obtained with a yield of 1%–2% in benzene at 70 °C in the presence of 2,2'-azobis(isobutyronitrile) as an initiator. The copolymerisation of $(\mu\text{-H})\text{Os}_3(\mu\text{-4-VPy})(\text{CO})_{10}$ with styrene or acrylonitrile under the same conditions resulted in the incorporation of up to 3% of cluster units into the polymeric chain without noticeable changes in the structure of these clusters. The IR spectra of the cluster

carbonyls are virtually indistinguishable from the spectra of the corresponding initial monomers (Table 3), though some minor changes in the intensity and widening of individual absorption bands may still be revealed. Apparently, the conjugation of the double bond in $(\mu\text{-H})\text{Os}_3(\mu\text{-4-VPy})(\text{CO})_{10}$ leads to the redistribution of the electron density in the Os–Os bonds and the decrease in their length. In the polymer, this conjugation disappears, and the photoelectron spectra of the framework become close to those of the unsubstituted cluster $\text{Os}_3(\text{CO})_{12}$. Kinetic studies showed that each polymeric chain ($\overline{M}_n = 5\text{--}37$ kDa) contained, on the average, one cluster unit and one terminal double bond.²⁶³ This implies that the binding of the Os_3 -containing monomer to the growing macroradical inhibits the chain growth (Scheme 15). This



Scheme 15

Table 4. Composition and characteristics of cluster-containing copolymers.

First component (M ₁)	Second component (M ₂)	Molar composition of monomeric mixture M ₂ : M ₁	Fraction of units with preserved cluster framework (mol.%)	$\overline{M}_w/\overline{M}_n$	Note
	Styrene MMA <i>N</i> -[tris(hydroxymethyl)methylacrylamide]	99 : 1 99 : 1 99 : 1	3.7 1.0 1.6	14720/6400 44700/21300 —	
	Styrene MMA <i>N</i> -[tris(hydroxymethyl)methylacrylamide]	99 : 1 99 : 1 99 : 1	1.3 1.8 1.6	16900/7200 41300/24600 —	
	Styrene MMA <i>N</i> -[tris(hydroxymethyl)methylacrylamide]	98.8 : 1.2 99 : 1 98.5 : 1.5	1.4 1.1 1.5	3320/2250 18500/10060 7000/5500	
	Styrene AN	(99–99.5) : (0.5–1.0) (99–99.5) : (0.5–1.0)	0.2–1.0 0.1–0.2	—/5000–36500 —/1500	In mass In benzene
	Styrene AN	(99–99.5) : (0.5–1.0) (99–99.5) : (0.1–1.0)	0.1–1.0 0.1–1.0	—/12000–25500 —/8000–26000	In mass In benzene
	Styrene AN	(99–99.5) : (0.5–1.0) (99–99.5) : (0.1–1.0)	0.1–1.0 0.1–1.0	—/21000–26000 —/15000–17000	In mass In benzene
[Mo ₆ Cl ₆ (<i>N</i> -VI)](CF ₃ COO) ₄	<i>N</i> -Vinylimidazole (<i>N</i> -VI)	(99–99.5) : (0.5–1.0)	0.1–0.5	—	Comonomer as a solvent

does not however lead to the decrease in the concentration of active species owing to the fast transfer in the chain.

The role of chain transmitters may be played by both styrene and comonomer containing Os_3 ; however, as in the case of homopolymerisation, the steric hindrances impose certain restrictions on the chain transfer reaction onto the cluster monomer. Therefore, the role of this reaction is insignificant. It is most probably that the chain transfer is realised only *via* styrene. The analysis of the molecular mass characteristics allowed the estimation of the constant of the growing radical interaction with the double bond of the cluster monomer.²⁶⁴ The lower limit of this parameter is within the range of 40 to 300 litre $\text{mol}^{-1} \text{s}^{-1}$. Similar features were revealed for the copolymerisation of Os_3 -containing monomer with acrylonitrile.

The copolymerisation of $\text{Rh}_6(\text{CO})_{15}(4\text{-VPy})$ with styrene in toluene occurs much easier,²⁶⁵ and the content of the cluster monomer may be as high as 10%. This seems to be due to the fact that 4-VPy is linked to the cluster framework only by a donor-acceptor bond.

It may be assumed that the size of the metal-containing cluster particles is not much larger than that of the initial clusters, especially at their low levels in copolymers since the polymeric segment formed from the comonomer is a stabilising factor preventing associative processes. This view is supported by the direct evidence provided recently from a study²⁵³ of the radical block copolymerisation of staphylnuclear monomers in solubilising monomeric media with $[\text{Mo}_6\text{Cl}_6(\text{N-VI})_6](\text{CF}_3\text{COO})_4$, where N-VI is *N*-vinylimidazole. *N*-Vinylimidazole acts simultaneously as a solvent for the cluster monomer (at 0.1 and 0.5 M) and as a comonomer. At 70 °C, fast homogeneous copolymerisation took place with subsequent cross-linking and thickening of the reaction medium, which contained the chemically bound monodispersed clusters at a relatively high concentration. The sizes of the polymer-immobilised staphylnuclear and the initial clusters were close and amounted ~ 1 nm. Apparently, one should agree with the view of Golden *et al.*^{252,253} who believe that the use of monomers as solvents may become a common practice in the preparation of polymer-immobilised monodispersed metaloclusters.

The incorporation even of small quantities of cluster monomers into a copolymeric chain improves the parameters characterising the resistance to destruction of both the metalocluster itself and the polymer. For example, the Os_3 -copolymers manifest mutual stabilisation of PS and PS-bound clusters.²⁶⁶ The decarbonylation of clusters begins at ~ 200 °C, while the decarbonylation temperature of copolymers is higher by ca. 150 °C. The thermal resistance of clusters is increased only when they are bound with a polymeric chain, while in mechanical mixtures this effect is absent. One of the major reasons for this phenomenon may be the transfer of energy at increased temperatures from the rotational-vibrational degrees of freedom of the cluster to the translational degree of freedom of the polymeric chain segments. The decomposition temperature of the polymers comprising metaloclusters is in turn increased by 50–60 °C, while the effective activation energy of thermal destruction is increased by 40–60 kJ mol^{-1} . The vitrification temperatures of polyvinylimidazole and of its copolymers with an imidazole staphylnuclear cluster at concentrations of 0.1 and 0.5 M are 164, 220, and 257 °C, respectively.²⁵³

Despite the sparse character of the data on the polymer-immobilised clusters prepared *in situ*, the recent progress in this direction promises the obtaining of new data and their systematisation.

The above statements referred to the preparation of polymer-immobilised clusters by polymerisation. There are no principal obstacles preventing the use of polycondensation reactions for this purpose. In all cases, the principal difficulty resides in the synthesis of appropriate metallomonomers with bi- or poly-functional ligands. The role of such ligands may be played by the groups capable of binding active hydrogen from diols, diamines, and other compounds.

The high diversity of reactions of substitution or exchange between the functional groups of reagents makes this approach rather promising. The synthesis of these polymer-immobilised clusters may also rely on the use of cluster-containing compounds with the ligands comprising epoxy or other (*e.g.*, ethyleneimine) cycles, isocyanate groups (*p*-phenylenediisocyanate, 2,4-toluylene-diisocyanate), *etc.*⁸ This method allows the preparation of cluster-containing polyurethanes, polyamides, polyesters, and polyepoxy compounds.

Naturally, the controlled pyrolysis of polymer-immobilised clusters yields highly dispersed metal powders, while the pyrolysis of heteronuclear polymer-immobilised clusters may potentially be a suitable technique for producing nanometre-sized powder alloys (similarly to the pyrolysis of initial $\text{HFeCo}_3(\text{CO})_{12}$, $[\text{Co}(\text{MeCO-Me})_6][\text{FeCo}_3(\text{CO})_{12}]$,²⁶⁸ *etc.*). One should not rule out that this approach may be beneficial in the development of the solid-phase method for reducing metal oxides (it is known²⁶⁹ that if the contact between reagents is close, the reduction of Ag_2O in graphite is realised at temperatures as low as 100–200 °C). The incorporation of Pt clusters into a glass-carbon matrix was carried out by immobilisation of mononuclear complexes of (ethylene)-bis(triphenylphosphine)platinum(0) on the triple bonds on poly(phenylenediacetylene) oligomer.²⁷⁰ On heating to 600 °C, the toluene-soluble complex of composition 1:4 or 1:2 yields a Pt-enriched glass-carbon in the form of thin films with a narrow distribution of Pt clusters with a mean diameter of 1.6 nm. The structure of these clusters is shown in Fig. 10. Interestingly, the non-immobilised complexes form large Pt particles 600 nm in diameter. The ceramics of general formula $\text{M}_x\text{Si}_y\text{C}_z$ ($\text{M} = \text{Fe}, \text{Co}$) are produced by the pyrolysis of cluster-containing diacetylene oligomers at 1350 °C.²⁷¹

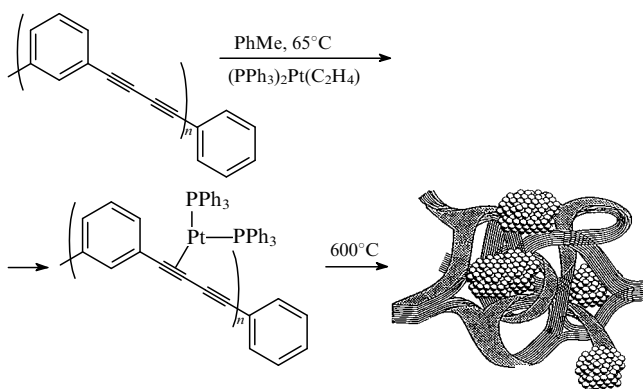


Figure 10. Structure of a Pt–poly(phenyldiacetylene) oligomer.

VI. Nanometre-sized particles, clusters, and polynuclear structures immobilised in biopolymers and their analogues

The interaction of metal ions and nanoparticles with biopolymers and cells plays a highly significant role in the enzymatic catalysis, geobiotechnology, and bihydrometallurgy. Of practical interest for the geomicrobiological transformation of heavy metals are natural and genetic-engineering microorganisms the vital activity of which occurs under extreme conditions (high temperature and pressure, highly acidic or basic media, strong salinity, the presence of metals at levels toxic for common microorganisms). By analogy with thermophiles, halophiles, acidophiles, *etc.*, a group of microorganisms is named metallophiles.^{272–276}

§ Recently, platinum – gold phosphine clusters with isonitrile ligands of the type $[\text{Pt}(\text{RNC})(\text{AuPPh}_3)_8]^{2+}$, $[\text{Pt}(\text{CO})(\text{AuRNC})(\text{AuPPh}_3)_7]^{2+}$ have been synthesised.²⁶⁷

It is believed²⁷² that the extent of selective metallophilicity of microorganisms is determined by a number of factors: the selective direction of motion of the colloidal particles relative to microorganisms, the nature of chemical fixation of particles on the surface and its strength, *etc.* Among the bonds formed, the covalent ones are predominant.

A consequence of selective metallophilicity is a genetically predetermined specialisation of microorganisms for the interaction with definite metals. This results in the appearance under natural conditions of a rigorously determined system including a cell of definite species and a metal (or a group of related metals).²⁷² Flocculation of cells by colloidal metal particles leads to the formation of rather large (up to 50–60 μm) bioskeletal aggregates undergoing sedimentation in aqueous media. Specific NADH oxidase, the protein capable of incorporation of gold into the active centre, has been isolated and characterised recently. Its molecular weight is 600 000, and it contains three metal atoms per mol of protein.

In addition to bacteria, the binding of metals is effected by yeasts, fungi, numerous algae, and some Protozoa, and this largely extends the potential of biochemical transformation and transfer of metals under natural conditions.

One of the manifestations of the colloidal-chemical binding is the coagulation of metal sols (in particular, the best studied is the gold sol that is characterised by the simplicity of its preparation and a relatively high stability, see above). The heterocoagulation of these sols results in the formation of biopolymer-immobilised nanoparticles or, in other words, mixed aggregates of living microorganisms and nanoparticles. Many of them possess specific properties that are apparently determined by the processes occurring in the diffusion layers of cells and are associated with the electrical heterogeneity of their surface.²⁷⁷ These processes induce the binding of sol particles and simultaneously decrease the threshold of their coagulation due to the increased concentration of counterions. These highly dispersed biogenic aggregates are widely distributed in nature as economically important metal ores, the sole of sedimentogenesis facies,²⁷⁸ *etc.* Furthermore, the very idea of immobilisation of metal complexes on polymers is largely borrowed from natural systems.

1. The pathways of formation of metallobiopolymeric systems

The peculiarities of the interaction of microorganisms with metal sols, as a rule, largely depend on the nature of the metal. In this respect, the best studied systems are the colloids of gold,²⁷⁶ the colloids of other noble metals, as well as those of iron, copper, and manganese have been investigated to a lesser extent. Biosorption is the novel approach to the metal recovery from the dilute solutions. It was shown that microorganisms and algae allow the extraction of up to 100% of lead, mercury, zinc, nickel, cobalt, manganese, chromium, uranium, and some other elements, up to 96%–98% of gold and silver, up to 84% of platinum, 93% of selenium from dilute solutions. It is shown also that bacterial polysaccharides are effective in the recovery of radioactive elements, as well as of copper and cadmium, from solution (Table 5).²⁷⁹

The bacterial concentration of metals is preceded by their adsorption on the cell surface with subsequent assimilation.²⁸⁰ This can be accompanied by enlargement of sol particles (flocculation) and the adsorption and deposition of a coarse metal-bacterial mass (heterocoagulation). Like in the systems based on synthetic polymers, the sol with particle size of ~ 10 nm proves to be the most stable.

An important distinctive feature of the colloid-bacterial interaction is the diversity of the forces involved with mechanisms of electrostatic, molecular, and chemical origin. The preferential adhesion between colloidal particles and associations of bacterial cells is observed at sites of their contact. For example, the coccal bacteria *M. luteus* with the mean size of 2000 nm isolated from an auriferous placer form packages of 4–8 cells that sorb effectively the gold particles (up to 10 mg of Au per 1 g wet biomass),²⁷⁶ but

Table 5. Sorption of metals by microorganisms.²⁷⁹

Metal sorbed	Microorganisms	Metal content (mg) per 1 g dry cells mass
U, Th	Denitrifying bacteria	140
	<i>Rhizopus arrhizus</i>	180
U	<i>Pseudomonas aeruginosa</i>	≤ 560
	<i>Saccharomyces cerevisiae</i> ,	100–150
	<i>Pseudomonas aeruginosa</i>	
	Biosorbent M (<i>Penicillium chrysogenum</i>)	80–120 (purification of waters containing < 0.05 mg litre ⁻¹ of elements)
Ag	Bacterial community of <i>Ps. maltophilia</i> , <i>Staphylococcus aureus</i> and unidentified forms	≤ 300

do not induce heterocoagulation; in this situation, one cell binds, on the average, 10^4 colloidal gold particles.

At least in the initial stages, the interaction is reduced to the electrostatic binding, and it is this fact that explains the reversibility of heterocoagulation:²⁸⁰ after the introduction of the protonophore into the incubation medium, the dispersed metal particles are released from the cell surface. In general, there are two routes for the realisation of this process. In cell associates, further concentration of particles occurs at the sites of their contact, which is accompanied by their enlargement. In single cells, the increase in the particle size is not preceded by aggregation: the particles formed in the process of concentration are gradually rejected by the cell surface.

Most probably, the electrostatic and chemisorptional attachment of colloidal particles of metals and their compounds to the cell surface occurs mainly due to the products of its metabolism including such functional groups as $-\text{S}-$, $-\text{COO}^-$, $\text{PO}(\text{OH})\text{O}^-$, $-\text{NH}_3^+$. It is significant that, in contrast to positively charged proteins (trypsin, papain, lysozyme, RNase),²⁸¹ the negatively charged proteins (human serum albumin, soybean trypsin inhibitor) do not cause flocculation of gold particles. Lysozyme manifests special properties: the flocculation of sol on it occurs in a narrow range of enzyme concentrations ($1-10$ $\mu\text{g ml}^{-1}$), while its higher levels stabilise the sol and enhance the aggregational stability of the system, on the whole. The occurrence of consecutive stages of flocculation and stabilisation of metal colloids with the increasing concentration is also characteristic of certain synthetic polymers, such as polyethyleneimine and non-ionogenic polyethyleneoxide.

Let us note some differences in the behaviour of proteins and synthetic polymers. First, proteins differ in their selectivity towards different dispersed phases in the course of flocculation which is determined not only by electrostatic factors but also by specific binding of these phases by functional groups of amino acid residues, especially by the sulfhydryl and amino groups.²⁸² In particular, the addition of *p*-chloromercuribenzoate, which specifically blocks the SH groups of proteins, was found to decrease their flocculating activity. Second, the native structure of the biopolymer is of prime importance for the sorptional processes to occur. For example, partial destruction of the polysaccharide skeleton of bacterial cell walls (by lysozyme) reduces considerably their sorptional ability.

The cells of monoculture tissues (*Pseudomonas sp.*, *Bacillus cereus*, *Bacillus sp.*, *Bacillus subtilis*) grown under similar conditions differ significantly in their ability to accumulate metal particles on their surface. The accumulative ability of cells was observed to correlate with the flocculating capacity of preparations isolated from them (Fig. 11).²⁸³



Figure 11. The cell of associate tissue culture in the presence of colloidal gold particles ($\times 35\,000$).²⁸³

There is experimental evidence for the binding of metal particles on the surface of cells by their carbohydrate or glycoprotein structures. A glycoprotein with a molecular weight of ~ 50 kDa providing for the binding of colloidal gold was isolated from different cells (including *B. subtilis*) by extraction with butanol. The specificity of binding of different compounds by this protein decreases in the series $\text{Au} \gg \text{Pt} > \text{MnO}_2 > \text{Al}_2\text{O}_3$.

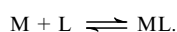
The liposomes (which are the closest models of biomembranes having no effect on the aggregative stability of gold) modified by this glycoprotein sorb actively particles of metals. Apparently, the glycoprotein is bound with lipids in the bacterial cell wall. As a matter of fact, it is the increased level of glycopospholipids in them and the extended branching of fatty acid residues that determine the ability of the above-mentioned *M. luteus* cells to survive under extreme conditions (at high Au concentration).²⁸⁴

Following the adsorption and heterocoagulation of colloids in biopolymers, the recrystallisation and enlargement of dispersed metal particles occurs on the surface of living cells. These processes result from the occurrence of intense oxidation–reduction of metals. In case of gold, at the first stage, the colloidal gold particles are oxidised possibly by hydrogen peroxide generated by cytochrome C, while the second stage involves the endogenous reduction of gold ions with the participation of the plasma membrane.²⁷⁶ This may occur only at a sufficiently intense ion flux. The cationic $-\text{NH}_3^+$ groups are believed to be responsible for the solubilisation (oxidation) of gold by the *Bacillus subtilis* cells, whereas the anionic carboxyl and phosphoryl groups are responsible for the reduction of complexes of gold with metabolic products.²⁸⁵

Thus, in the system ‘biopolymer–colloidal gold particles’, the latter are redissolved to eventually form larger particles.

The mould fungi are known to reduce gold to its metallic state.²⁸⁶ Sometimes, these transformations also involve humic and fulvic acids. As a result, a specific ‘depot’ of bioelements is formed.²⁸⁷

The surface of bacteria may contain several independent metal binding sites (M). This process is described by the equilibrium



The symbol L designates the binding site on the bacterial surface, while ML stands for the ‘bacterium–sol particle’ complex. The total number of binding sites (n), the quantity of bound metal particles (v), and the association constant $K = [\text{ML}]/[\text{M}][\text{L}]$ may be calculated by the Scatchard equation:²⁸⁸

$$\frac{v}{[L]} = nK - vK.$$

For example, the *M. luteus* cells have two types of independent gold-binding sites:²⁷⁶ in the first type of sites (hydrophilic), the binding occurs as a result of electrostatic interaction ($K_1 = 3.85 \times 10^9$ litre mol⁻¹, $v_1 = 4.7 \times 10^3$), in the second type of

binding sites it goes occurs *via* an oxidative process of the formation of gold complexes ($K_2 = 4.6 \times 10^8$ litre mol⁻¹, $v_2 = 4.3 \times 10^3$).

The model of bacterial concentration and crystallisation is rather complicated. The process may proceed *via* fusion (assimilation) of small (10–20 μm) needle-like crystalline polygons, which bind to each other to form visible gold grains extracted by the gravimetric method. In addition, the colloidal particles may play the role of crystallisation centres as nuclei of a new phase under conditions of continuous cooperative oxidation and reduction of the metal ions formed. Apparently, the transformation of endogenous gold under conditions of placers formation follows the same mechanism.[¶]

The processes of accumulation of heavy metals by cells occupy a special place. It is known that the most important cell components are the low-molecular-weight (5–10 kDa) metal-binding proteins thioneins, rich in SH groups, which accumulate both the metals essential for the cell (Cu, Mn, Fe, Co, Cr, Mo) and unessential ones.[†] The macromolecules of these proteins consist of two separate subunits. Each of them binds metal ions into a polynuclear metal-thiol cluster surrounded by cysteine residues. For example, Cd- and Zn-thioneins contain 7 metal atoms each, of which four are bound with 11 cysteine residues ($\text{M}_4\text{Cys}_{11}$) in a C-terminal A-cluster, while 3 metal atoms are bound with 9 cysteine residues (M_3Cys_9) in the N-terminal B-cluster.²⁹¹ At the same time, Ag and Cu form M_{12} metallothioneins containing 6 metal atoms in each domain.

The biological function of thioneins is, most likely, the storage and detoxification of heavy metals and possibly in the provision of the resistance of microorganisms to them.²⁹² Apparently, the accumulation of metals is associated with intense reduction, localisation, and adhesion on the outer membrane of metal particles formed. During the period of adaptation, the cells can acquire a plasmid of resistance to the metal, and this capacity is realised through the intensification of the reduction of metal ions. Thus, natural selection may result in the formation of metal-tolerant microbial strains.

The analysis of the immobilisation of nanoparticles on biopolymers allows one to note two aspects. First, most of the heavy metals bind simultaneously to several protein macroligands with a specific spatial environment and conformation. Triple complexes may also form, *e.g.*, protein–M–nucleic acid ($\text{M} = \text{Au}, \text{Pt}, \text{Pd}$).²⁹³ Possibly, it is the presence of these formations that provides the anticarcinogenic effect achieved upon introduction of these metals into organisms. Second, heavy metals, *e.g.*, Au(I) react with mixed-metal thioneins (with native Zn-, Cd-, and Co-thioneins) by replacing selectively Zn and even Cd when added in excess. This process is characterised only by minimal changes in the protein conformation.

Metalloclusters play a very important role in the processes of bacterial mineralisation,^{294–296} and their investigation is the subject of a new branch of science called bioinorganic solid-state chemistry. Its topic is the study of the formation and structure of nanoscale materials in biological environment. A characteristic example is the formation of nanoparticles on the base of ferritin (Fig. 12).²⁹⁷ A nanoparticle of Fe_3S_4 is deposited in the inner part of the protein shell as a result of chemical transformations under mild conditions. The process is still more simplified when a ‘metal-free’ apoferritin is used for this purpose. For example, the biopolymer-immobilised Mn^{3+} oxides 8 nm in diameter are obtained upon oxidation Mn^{2+} to Mn^{3+} . This route is also effective for the preparation of nanoscale biomaterials based on Ag_2O and especially of calcium phosphates ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, $\text{Ca}_8\text{H}_2(\text{PO}_4)_6$, *etc.*) which are important components of osseous

¶ The solubilisation, deposition, and formation of new layers of gold on the surface of initial grains is characteristic of the entire history of hypergenic native gold.²⁸⁹

† Deposits of iron and manganese, which are highly important for functions of living organisms are mostly of biogenic origin.

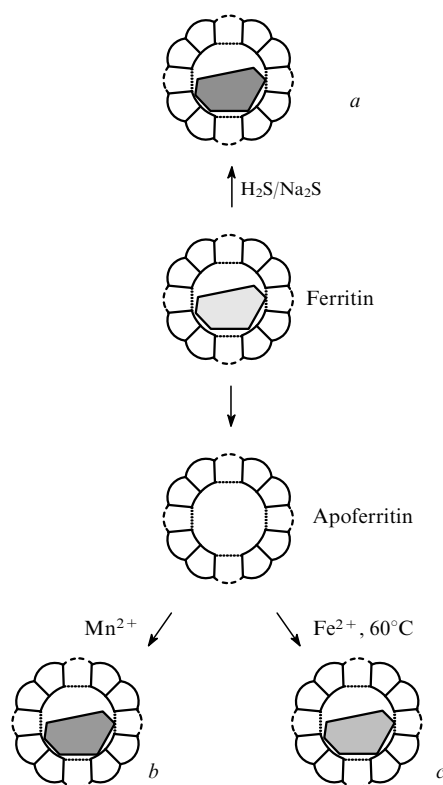


Figure 12. Synthesis of nanophase materials based on ferritin: (a) Fe_3S_4 ; (b) Mn_2O_3 ; (c) Fe_3O_4 .

tissues. Special attention should be given to the intraferritin formation of *in situ* deposits of Fe_3O_4 with definite crystallochemical characteristics.²⁹⁸ This leads to the formation of ferromagnetic proteins,[‡] which are used to prepare magnetic images for clinical purposes. The complexity and precision of such bioinorganic reactions require strict ordering of the particles formed with regard to their size and morphology which are difficult to achieve under laboratory conditions.

Some heterometallic clusters of ferredoxin with the composition $[\text{MFe}_3\text{S}_4]$, where $\text{M} = \text{Zn}, \text{Co}, \text{Mn}$, are known. They are present, in particular, in the *Pyrococcus furiosus* cells. It is believed²⁹⁵ that bacterial methods may be effective in the preparation of finely dispersed precursors of superconducting high-temperature ceramics and other materials.

Metalloprotein preparations are quite often used in medicine to regulate the enzyme activity and to devise new drugs of narrow targeted action.³⁰⁰ Colloidal compounds of calcium and magnesium with plant proteins are employed for the regulation of gastric juice acidity, a finely dispersed Fe_3O_4 complex with serum albumin is administered intravenously as a contrasting compound for X-ray studies, *etc.* Colloidal gold and its biopreparations have been used since ancient times as medicaments, many of them are known to be effective antiarthritis drugs. Colloidal gold is widely used in immunochemical studies as an electron-dense cytochemical marker in electron microscopy. The hydrophobic character of gold particles and the existence of electrostatic charge on their surface have allowed the development of specific markers with numerous macromolecules, such as antibodies, lectins, enzymes, various proteins, glycoproteins, and polysaccharides.³⁰¹

‡ This is clearly seen in electron micrographs of bacterial magnetite,²⁹⁹ an intracellular product composed of Fe_3O_4 crystals arranged in a chain parallel to the longitudinal axis of *Coccus* and *Spirillum* bacteria (Fig. 13). Such magnetically ordered (magneto-tactical) bacteria may orient themselves (move) even in weak (0.25–0.5 G) magnetic terrestrial fields by performing the 'navigational' functions in living organisms.

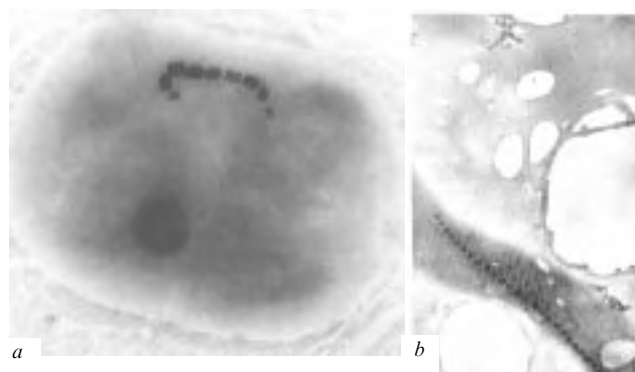


Figure 13. Electron micrographs of *Coccus* bacteria with a chain of nine intracellular magnetic crystals (a) and *Spirillum* cells with a chain of cubic-octahedral crystals (b). The cell length is 3 μm , the size of each crystal is $\sim 50 \times 50 \text{ nm}$.

Special attention should be paid to the microbial geotechnology, *i.e.*, to the extraction of metals from their ores, concentrates, embedding rocks, and solutions by means of microorganisms and their metabolites.²⁷⁹ The bacterial leaching of copper and uranium has long been used in the industrial scale. This process includes fragmentation of ores and preparation of pulp, bacterial leaching of the target metal, filtration, neutralisation of solid residues, and cyanation. The colloidal-biochemical basis has been elaborated recently for the detoxification of cyanide-containing wastes.³⁰²

2. Polynuclear metalloenzymes

All metal-containing protein systems important for biocatalysis and metabolism are divided into four main groups:³⁰³ enzymes (containing Mn, Fe, Co, Cu, Mo), redox proteins, transport, and storage systems (which regulate the concentration of metal(s) at specific sites of the organisms). Kidney proteins, which bind and withdraw heavy metals from living organisms, are also sometimes classified in these groups. The biological functions of these proteins and the types of interactions in them have been reviewed.³⁰⁰

The most typical representative of storage proteins is ferritin. This iron-storing protein contains 24 identical subunits with an inorganic core composed of 4500 iron atoms in the form of basic hydrophosphate $(\text{FeOOH})_8(\text{FeO}-\text{OPO}_3\text{H}_2)$ and having a diameter of 7.3 nm (such a structure is similar to that of synthetic polymers considered above) (Fig. 2).³⁰⁴

The distinctive feature of this large group of redox biocatalysts is the presence of several interacting atoms of transition metals in one protein molecule. Nowadays, over 100 enzymes are known that include several atoms of iron, copper, molybdenum, or manganese, and in many of them the arrangement of atoms in polynuclear ensembles has been established. This refers especially to the metalloproteins containing non-hem iron complexes linked by oxy-, hydroxy-, and alkoxy-bridges.^{7,8,305} Binuclear iron complexes (with the $\text{Fe}_2\text{O}(\text{OCOR})_2$ core) were found in hemerythrin, ribonucleotide reductase, and acid phosphatase. Polynuclear $\text{Fe}^{2+}\text{Fe}^{3+}$ complexes are supposed to exist in numerous enzymes; the Fe_2S_2 groups, in ferredoxin; the high-nuclearity oxo-centres of iron, in the iron-storage proteins of ferritin and hemosiderin type, and in the magneto-tactic microorganisms mentioned above.

In the processes of biological nitrogen fixation, the active enzyme form is produced with the involvement of two components, iron- and iron-molybdenum-containing proteins (including 32–34 Fe and 2 Mo atoms), under the action of natural electron donors (ferredoxins, flavodoxins) in the presence of ATP. The molybdenum nitrogenase cofactor may possibly have the structure $\text{MoFe}_6(\text{SR})_6\text{L}_3$; the MoFe- and VFe-proteins (nitrogenases) were isolated from *Azotobacter vinelandii* and *A. chroococcum*.⁸

Enzymic photosystems that are employed for the liberation of oxygen from water comprise polynuclear complexes containing a cubane-like manganese core Mn_4O_2 ³⁰⁶ immobilised on the protein complex by means of carboxyl groups. Of other bimetallic systems, the Cu^{2+} – Zn^{2+} -containing superoxide dismutases, Cu_2Co_2 -superoxide dismutases, and some others deserve mention. The advantages of these structures with shared nuclear frameworks have been analysed in detail.^{7,8} Biopolymers including clusters with nuclei of Rh_6 ,³⁰⁷ Ru_3 ,³⁰⁸ Fe_4 ,³⁰⁹ and other are described.

Extensive studies of synthetic oligopeptide models of complexes may provide additional information on the mechanisms of action and routes of electron transport in native proteins.

VII. Major fields of the application of polymer-immobilised metal nanoparticles and metal clusters

As noted above, these species have found applications in diverse, sometimes unexpected fields of chemistry, physics, and biology, which largely stimulates their further studies.

The interaction of nanoparticles or clusters with traditional polymers improve their physicochemical properties and performance. This is explained by the ability of these particles to form ionic and coordination cross-links, restricting the mobility of molecular chains or their segments, by cohesive and adhesive interactions, and by other reasons.

The incorporation of metal nanoparticles into a polymer (polymeric shell) may lead to changes in the properties primarily of the polymer matrix itself and also of immobilised nanoparticles or clusters (in particular, to their passivation). An in-depth analysis of these changes goes beyond the scope of this review, and we shall dwell here only on the most essential ones.

1. The modifying effect of nanoparticles on polymer matrices

Virtually all of the methods used to prepare polymer-immobilised nanoparticles are associated with the metal–matrix interaction, especially at the interface. The incorporation of even such a small species as a nanoparticle perturbs substantially the polymer structure.³¹⁰ The extent of structural changes depends on the concentration of nanoparticles, which are the knots of the emerging structural network. The presence of as little as 1% of highly dispersed $\text{Fe} + \text{FeO}$ mixture resulting from the decomposition of iron oxalate in HPPE alters the sizes of the structural element of the polymer, increases the density of the fluctuational network of molecular anchoring and the proportion of oriented polymeric chains.³¹¹ This results in a considerable increase in the impact elasticity of the material, its tensile strength, and resistance to cracking. The processes of structuring in the polymer phase in the presence of nanoparticles occur in different ways. The interaction of nanoparticles with each other (especially at their high concentrations) leads to the formation of coagulation structures. At low levels of nanoparticles, when the formation of coagulation structures is impossible, the polymer matrix itself undergoes structure changes. These processes are accompanied by changes in the temperatures of vitrification, fluidity, thermal destruction, and in the thermomechanical parameters (as a rule, towards their enhancement), which is connected, as noted above, with the restricted mobility of macromolecules due to their interaction with the surface of nanoparticles, and also with the formation of secondary structures.

Thus in the Claspols (see Section IV) obtained by the thermal decomposition of metal salts and carbonyls in polymers melts (PE, PTFE, *etc.*) particles appear that reduce the mobility of molecular chains and increase thereby the thermal resistance of polymeric compositions.³¹² As noted above, the decomposition of a fine dispersion of palladium hydroxide in PVC leads to the formation of network structures containing in their knots the highly dispersed metal thereby raising the temperature of the complete dehydrochlorination of the polymer.¹³¹ The nanoparticles produced by the thermal degradation of copper oxalate increase the

size of the polyamide crystallites, the interaction energy between the structural elements, and strength, but they reduce the overall degree of the polymer crystallinity.¹²⁶ The water of crystallisation released during the decomposition of cadmium oxalate trihydrate accelerates the crystallisation of structural elements, decreases the cohesion energy, and leads to a looser polymer matrix. The π -complexes of iron tricarbonyl with polystyrene-butadiene block-copolymers influence, in the temperature range of their softening, the segmental mobility of the polybutadiene microphase and even when present at levels below 2 mass % Fe they manifest an ordering effect, which increases the macromolecule rigidity.³¹³ At higher metal concentrations, this effect is enhanced owing to the development of a physical network. The dispersed metals formed *in situ* appear to be promising modifiers of the polymer fluidity.¹⁸⁸ Of special interest is the method of ‘non-chain’ inhibition of the thermo-oxidative destruction of temperature-resistant polymers³¹⁴ based on the binding of oxygen by highly effective acceptors, metal nanoparticles formed directly in the polymer matrix.

There are numerous examples of the improvement of adhesive properties of the systems under discussion.³¹⁵ The tribological coatings (of Ni–PTFE type) are characterised by the homocoagulation interaction between the polymer and nanoparticles at the moment of their isolation on the electrode.¹⁷⁶

2. Electrical and magnetic properties

Various atomic and electronic processes that occur at the interface in polymer–nanoparticle composites largely determine their unique properties. These materials become electrical conductors only at definite ratios of the components when conducting chain-type coagulation structures and not matrix systems are formed. In other words, the role of current-conducting channels is played by the fractal clusters⁵⁴ formed upon cohesion of nanoparticles. The highest conductivity is attained when the metallopolymeric material is permeated by interconnected chains of contacting conducting particles, *i.e.*, when it has a percolational structure. As a rule, this is achieved at a content of nanoparticles of ~50 vol. %.

These materials find extensive uses in microelectronics (in the production of connecting circuit boards, flexible cables, *etc.*), in the production of highly dispersed conducting coatings, and in the film and membrane technology. They are also applied as precursors in the preparation of superconducting ceramics. Materials with the superconductivity transition temperature of 90 K were obtained on the basis of Y-, Ba-, and Cu-chelates of polycondensation type.³¹⁶ This temperature is still higher (110 K) in the polymers with components of bismuth ceramics.³¹⁷

To prepare ultradispersed metal particles in polymeric matrices, nearly all of the methods described in Section IV are used, including the vacuum metallisation of polymers. The properties of these magnetic materials, ferroplastics or ferroelastics, namely, their magnetisation curve, magnetic permeability, coercive force, magnetic hysteresis loop, magnetostriction, *etc.*, depend on their prehistory, the nature of the polymer and the nanoparticles, concentration and structural state of particles and can vary over very wide ranges. For instance, the magnetic behaviour of the systems Ni–HPPE and Co–HPPE depends on the conditions of cryosynthesis.⁷⁸ At temperatures above 370 K, the irreversible interaction of Ni clusters with the matrix takes place in the Ni–HPPE system. In the Co–HPPE system, at 470 K the form of the thermomagnetic curve is completely changed due to the enlargement of Co particles.

The peculiarities of the magnetic behaviour of systems obtained by the reduction of metal salts in the medium of a swollen interpolymeric complex of polyacrylic acid with an urea–formaldehyde oligomer¹⁶⁴ and by the thermolysis of cationic complexes of iron arenecyclopentadienyl and arylencarborane oligomers^{72, 318} have been considered. Studies along the same lines were carried out with composites obtained by the thermal and oxidative decomposition of Co and Fe carbonyls in PVF

matrices,¹²⁰ and the hydrogen reduction of organocobalt precursors¹³⁴ and Ni carbonyl in epoxy resin films in different solidification conditions.³¹⁹ Interestingly, the conductivity and the percolation parameters of the latter system depend on the internal stresses arising during solidification.⁵³ Magnetic particles are rather often introduced in different gels: silicone,³²⁰ polyacrylamide,³²¹ polyethyleneoxide,³²² and other gels.⁷² The conducting Ag-containing films are produced by the reduction of AgNO₃ in PVAI.¹⁴⁴ Sometimes, ferroplastics are formed in magnetic fields (for example, neodymium ferrites, in 3–30 G fields), and then are subjected to mechanical (pressing,³²¹ processing on Bridgeman anvils⁷²), thermal,^{323, 324} and other³²⁵ impacts. In recent years, these studies are being developed extensively.

Of interest is the preparation of thin (3–7 nm) modifying magnetic coatings (that can be obtained, *e.g.*, by electrochemical deposition) on the surface of self-assembling thin films of the Langmuir–Blodgett type. Thus, the coatings including α -Fe (70 at.% Fe), magnetite Fe₃O₄, and admixtures of Fe₂O₃, may be formed on organosilanes.¹⁸² Polymer-immobilised particles are formed *in statu nascendi* in magnetic fields. These materials seem to be rather promising as drug carriers, for magnetic recording of information, magnetic separation, as materials possessing the magnetic-optical properties, and as magnetic fluids,³²⁶ the latter being colloidal solutions with strong magnetic properties. The role of carriers operating under extreme conditions (wide temperature range, vacuum, aggressive and biologically active media) may also be played by polymers, *e.g.*, oligoorganosiloxanes.

3. Polymer-immobilised nanoparticles as optical materials and semiconductors

The composite materials that comprise polymeric optical media and nanoparticles possess a unique set of the optical (in the visible light range) and semiconductor properties. The ease of mechanical processing and the film-forming properties of these materials make possible their use for the preparation of dispersive optical elements, band light filters, *etc.* To this end, the products of joint condensation of Au with a large excess of a diacetylene monomer, diphenylbutadiyne, or its polymer are most often used.⁶⁷ The metallopolymers produced contain 7%–16% of metal with a mean particle size of ~ 2 nm. The composite material is characterised by a 200-fold increase in the third-order optical coefficient. Thin films of Au- and Ag-plasmapolyfluorocarbon possess good optical properties.^{86, 90}

Homogeneous composite materials with high absorption and refraction indices suitable for the production of optical elements are prepared on the basis of polymeric glasses with sulfoselenides of transition metals, photochromic glasses with Ag and Cu halides, holographic emulsions of Ag halide nanoparticles in gelatin,³²⁷ *etc.* As a rule, the semiconductor component concentration in a polymeric binder (4-VPy, PVAI, *etc.*) does not exceed 0.1%, *i.e.*, ‘dilute solutions’ are used.

As in the synthesis of metal nanoparticles, the methods of the assembly of semiconductor components directly in polymeric matrices have found extensive applications. For example, nanocrystals of CdS and ZnS are obtained from their salts and H₂S in polymeric solutions. The content of cadmium sulfide (in the form of ~ 50 -nm particles) in these materials may be as high as 50%.¹⁷ It is known that the optical characteristics of gelatin films depend on the particle size of incorporated PbCrO₄.³²⁸ In this connection, it is noteworthy that the effective control of the particle size may be realised by varying the composition of copolymers and thereby the size of domains (Fig. 3) in ionomers.^{329, 330} Thus, the mean size of CdS particles in toluene solutions of the block-copolymer of styrene with acrylic acid increases from 1.8–2.3 nm to 3–5 nm as the number of acrylic units in the ionic block increases from 4 to 32. Note also good promises for the application of materials of this type in the systems for solar energy accumulation and transformation.^{331, 332}

4. The specific nature of catalysis with polymer-immobilised nanoparticles and clusters

The Group VIII metals in the colloidal state were among the first known catalysts of hydrogenation of organic compounds. As early as in the 1940s, PVAI, PVA, and PMMA were used to protect these colloids.³³³ Later, silk fibroin, nylon, PETF, *etc.* were used to this end.

Catalysts of this type are of prime theoretical interest since they allow modelling of the size effects on the catalytic activity. They may be used to exemplify many concepts of basic theories of the catalysis: A A Balandin multiplet theory, N K Kobozev theory of active ensembles, and D V Sokolskii theory of skeletal catalysis. Multiple attempts were undertaken to assess the influence of the catalyst particle size on its activity. For example, the size of nickel particles was varied from that of individual atom to the bulk metal.³³⁴ Quantitative estimates were made for the effect of the size of Ni_n/SiO₂ and Ni_nCu_m/SiO₂ on the course of hydrogenation.³³⁵ Similar studies were performed with regard to the behaviour of deposited polynuclear complexes in the processes of hydrogenation and isomerisation of alkenes.^{217, 336}

The application of polymer-immobilised cluster and nanoscale particles provides an additional possibility to shed light on the relationship between homogeneous, heterogeneous, and enzymic catalysis.⁴ According to some features, these particles are close to homogenous catalysts: they are obtained from ordinary, soluble metal compounds by increase in their nuclearity, the polymer often performs the functions of macroligand and stereochemical environment, they can function under mild conditions, *e.g.*, at temperatures below 100 °C. At the same time, these contacts also inherit major properties of heterogeneous systems: reactions occur at the interface, the activation of the substrate results from adsorption on the surface, the catalyst is easily separated from the reaction products and may be regenerated. The peculiarities of enzymic catalysis (substrate enrichment, structural correspondence, favourable orientation of reacting molecules, additional activation of the substrate by the multi-centre catalytic system, *etc.*) are also easily simulated using polymer-immobilised clusters and nanoparticles. For example, additional introduction of neodymium ions into ultradispersed Pd particles immobilised in water-soluble polymers exerts a promoting effect on these catalysts of acrylic acid hydrogenation.³³⁷ The reason for this effect consists in the substrate concentration resulting from the additional coordinational interaction with neodymium ions.

The above-discussed cryochemical technique for combining different elements, *e.g.*, Ag, Pd, or Pt with liquid oligo- and polyesters, and polydienes makes it possible to achieve the ‘critical loading’ of polymer (when the concentrations of metals exceed the coordination possibilities of polymers). Subsequent deposition of such polymer-immobilised nanoparticles on carbon powder may lead to the formation of Ag_n⁰/C, Pd_n⁰/C, and Pt_n⁰/C systems, which are traditional catalysts of numerous processes. Nanoparticles of Pt incorporated in glass-carbon matrices (Fig. 10) may also be referred to this type of catalyst.

In many cases, the polymer-immobilised nanoparticles manifest high activity and selectivity. This may be exemplified by the processes of ionic-coordinational polymerisation, hydrogenation, and oxidative transformations.⁵ The activity of these catalysts essentially depends on the nature of the polymer and the size of nanoparticles. After the removal of heavy Pt particles by centrifugation (20 000 rpm), the transparent supernatant containing about 20% of the initial Pt in a finely dispersed form manifests much higher activity in the catalytic reaction of hydrogen liberation from water.³⁷ The size of the remaining Pt particles is critical for their catalytic activity to be manifested irrespective of the nature of the protecting colloid.

Of special interest is the regioselectivity observed in the hydrogenation of undecenoic and oleic acids on clusters stabilised by surfactants or polymers.¹⁴⁸ The surfactant micelles surrounding a cluster not only stabilise it but also orient appropriately the

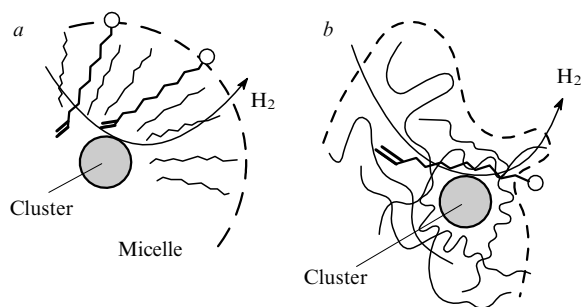


Figure 14. A supposed mechanism of the hydration of unsaturated fatty acids in micellar (a) and polymeric (b) systems.

unsaturated fatty acids (Fig. 14). In the case of a linear polymer, the double bond of substrate is more accessible to nanoparticles since the macromolecules are in a chaotic molecular motion.

The polymer-immobilised bimetallic Pt–Co colloids exhibit high selectivity (up to 99.8%) in the reaction of hydrogenation of cinnamaldehyde to the corresponding alcohol.²⁴⁷ The application of polymer-protected nanoparticles is expected to lead to the discovery of new specific effects in catalysis. The cluster $[\text{Pt}_{15}(\text{CO})_{30}]^{2-}$ fixed on Sephadex is used as the catalyst of the hydrogenation of selective redox-active cofactors.²²³

VIII. Conclusion

Among theoretical problems of the formation of clusters and nanoparticles in polymeric matrices, the most topical seem to be the questions of structural-morphological and spatial organisation of these systems at the local, molecular, and supramolecular levels, including thermodynamic peculiarities of their formation. Such an analysis has recently been performed using macrochelates as an example.³³⁸ The most important problem seems to be the stabilisation of nanoparticles by monolayers of polymers and Langmuir–Blodgett films. The number of studies carried out in this direction is clearly insufficient. Thus, the nature of the adhesion at the interfaces formed still remains obscure.

The passivation of nanoparticles formed should be realised within reasonable limits allowing preservation of their energy-rich state. A highly significant theoretical and practical problem is to learn to control the processes that occur on the surface or in a thin subsurface layer of polymer granules, films, or fibres. In this context, of interest is the preparation of self-assembling colloidal layers of Au, Ag, and Ag–Au on the surface of compounds of different origin (including the plasma-purified PTFE) premodified by hydrolysed alkoxy silanes containing functional groups.³³⁹ On such surfaces brought into contact with dilute solutions of monodisperse colloids, the assembly of nanoparticles takes place only as a monomolecular layer, which is 5–70 nm thick in the case of Ag and 5–20 nm thick in the case of Au and Au–Ag.

One may expect further progress in the development of novel methods for the preparation of polymer-immobilised clusters and nanoparticles. A promising direct synthesis of these products appears to be the dissolution of zero-valent metals in solutions of polymers that function as macroligands (like the solubilisation of metals in the presence of organic low-molecular-weight ligands)³⁴⁰ with subsequent recrystallisation of particles, as it occurs in biological systems (Section VI). The technique of stabilisation of nanoparticles and clusters in the course of polymerisation of micelle-forming monomers is likely to become practically significant. These methods have been devised using Pt clusters as models resulting from the photodecomposition of H_2PtCl_6 in the presence of monomers of the type of $\text{CH}_2=\text{CH}(\text{CH}_2)_8\text{COO}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3$.³⁴¹

It is only recently that studies of the formation of nanoparticles with polymer–polymer compositions have begun.¹ Hybrid PMMA–epoxy resin compositions and clusters of noble

metals have been prepared,³⁴² which are currently used as functional light-sensitive solid solutions and non-linear optical materials.

Formation of an inorganic phase $\text{Ti}(\text{OR})_4$ or $\text{Zr}(\text{OR})_4$ in copolymers of styrene and 4-vinylphenol (with the particle size ranging from 20 to 250 nm),³⁴³ preparation of nanoparticles by pyrolysis of metal carbonyls and mesogenic petroleum pitch,³⁴⁴ production of drug carriers composed of nanoscale particles,³⁴⁵ *etc.*, have been described.

Undoubtedly, the progress of research into such small particles requires further development and the application of modern physicochemical methods, including the visualisation of the surface structure at the atomic level by means of scanning tunnel microscopy, transmission electron microscopy, ferromagnetic resonance, small-angle X-ray scattering, X-ray photoelectron spectroscopy, *etc.*

The polymer-immobilised nanoparticles are already used to solve specific technological problems associated with the surface modification: its metallisation, the imparting of antistatic and magnetic properties to it, design of new materials for photo- and cinematography, design of efficient fibrous filtering materials allowing isolation and concentration of precious metals, *etc.* Specifically, the surface metallisation is required to decorate plastics,^{49, 310, 346} to modify polymeric films,³⁴⁷ to make tribological coatings, and other purposes. The coatings made of polymer-immobilised nanoparticles on the basis of Be and plasmopolymers have found unexpected applications in the reactions of thermonuclear synthesis.⁷⁹

It should be noted that clusters of metals can also be formed in such specific ‘polymers’ as fullerenes. In this case, both inclusion compounds of the type of endohedral complexes $\text{M}@\text{C}_{60}$, which are localised in the inner cavities of the spheroidal molecule C_{60} , and organometallic polymers of the type C_{60}Pd_n ,^{348, 349} or oligomers containing manganese carbonyls³⁵⁰ are formed.

Nanocomposite materials are also formed upon evaporation of metals in carbon nanotubes. The clusters of metals (Cr, Ni, *etc.*) are localised both inside these tubes and on their ends and surface.^{351, 352} On the other hand, the evaporation of metals in the oxidised nanotubes leads solely to the decoration of nanotube surface with nanoparticles (Fig. 15). An analogous pattern is also characteristic of lipid structures;³⁵³ their electrochemical polymerisation and metallisation result in metal-coated polymers having the shape of hollow cylinders several tens of microns long, $\sim 0.5 \mu\text{m}$ in inner diameter, and $\sim 50 \text{ nm}$ thick walls. Of interest is the similarity of such materials with the metallophilic microorganisms (Fig. 11).

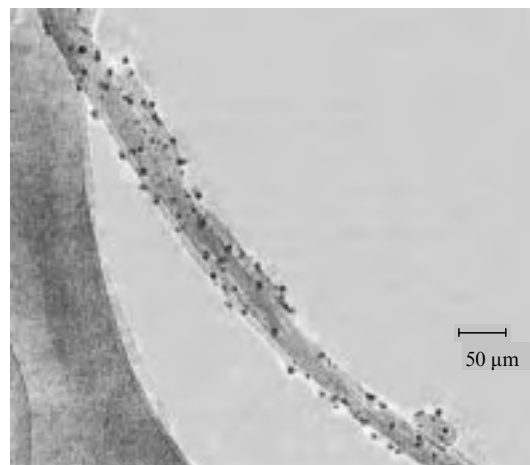


Figure 15. Electron micrograph of oxidised nanotubes decorated with silver.

Under mild conditions, biological systems bring about a controllable growth of iron oxide crystals (including magnetite) of definite size and morphology with strictly defined crystallochemical characteristics, which are so far difficult to achieve under laboratory conditions. Extensive studies of these processes (bio-inorganic solid-phase chemistry) will allow one to establish the basic principles of targeted synthesis of the products classed as 'crystal engineered'. The discovery of the phenomenon of selective aggregation of microorganisms with dispersed metals and their compounds has already laid the foundation for the methods of biotechnological enrichment used in metallurgy and for the environment protection. Many of these principles are employed in the rapidly developing field known as nanotechnology³⁵⁴ and are likely to form the basis of a new branch of science which may be defined as chemistry of highly organised compounds, including supramolecular chemistry and chemistry of hypermolecular compounds.³⁵⁵

* * *

Several publications related to the problems surveyed in this article have appeared since its submission. Of special note are an A.C.S. publication,³⁵⁶ a special issue of 'Chemical Materials' Journal,³⁵⁷ and a conference on electronic materials.³⁵⁸ The theoretical problems of stabilisation of nanoparticles by polymers have been discussed.^{359–366} Further development of the methods for preparation of polymer-immobilised nanoparticles^{367–378} and clusters^{379–382} has been documented. The research in traditional and novel fields of application of polymer-immobilised nanoparticles and clusters is in progress.^{371, 375, 383–394}

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Exogenous nitric oxide donors and inhibitors of its formation (the chemical aspects)

V G Granik, S Yu Ryabova, N B Grigoriev

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Abstract. The published data on the biological role of nitric oxide formed *in vivo* by enzymic oxidation of L-arginine are generalised. Special attention is given to exogenous nitric oxide donors, which can release NO *in vitro* and *in vivo* in oxidation, reduction, or hydrolytic cleavage. Also considered are the data on the chemical nature of inhibitors of NO-synthase responsible for nitric oxide formation from L-arginine. The bibliography includes 161 references.

I. Introduction

The discovery and verification of the mediator role of nitric oxide in living organisms have stimulated the search for drugs new in principle. Publications have appeared that were concerned primarily with the biological role of nitric oxide, problems of its insufficient or excessive release *in vivo*, and, correspondingly, the ways of increase or decrease in its content in organs and tissues.^{1–10}

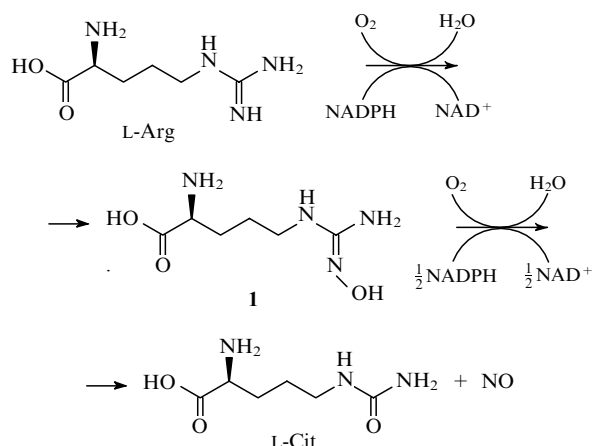
The present review generalises and considers the data on NO release from chemical compounds of different structure that can be combined under the common name of donors (or generators) of nitric oxide. In addition, the results of studies on inhibitors of isoforms of NO-synthase (NO-S) responsible for nitric oxide formation from L-arginine *in vivo* are discussed.

II. General aspects

Nitric oxide plays a crucial role in the functioning of the vascular system as an endogenous relaxant. The release of nitric oxide from endothelial cells of blood vessels results from an increase in the intracellular Ca^{2+} level, which initiates NO biosynthesis. Nitric oxide penetrates into neighbouring cells and activates soluble guanylate cyclase (SGC). The latter favours the transformation of

guanosine triphosphate (GTP) into cyclic guanosine monophosphate (cGMP). The increase in the cGMP level in cells causes the relaxation of vessels, eventually resulting in the lowering of arterial pressure. Other important biological functions of nitric oxide are: inhibition of platelet aggregation and effects on the immune system as well as on the central and peripheral nervous systems. Hence, NO plays the key role in the control of vascular tonicity and neuromediator mechanisms and exerts a cytotoxic and cytostatic action. A wide variety of pathological states (*e.g.*, cardiovascular, infectious, and inflammatory diseases, brain injuries resulting from insults, *etc.*) may largely be due to the elevated or lowered content of nitric oxide.

Biosynthesis of NO in the organism occurs *via* the oxidation of L-arginine and is catalysed by NO-synthase (NO-S) (for NO-S isoforms see below) with the participation of reduced nicotinamide adenine dinucleotide (NADPH) as an electron donor. NO-S contains one mole each of (6*R*)-5,6,7,8-tetrahydrobiopterin (BH_4), flavin adenine dinucleotide (FAD), flavin mononucleotide (FMN), and heme per monomeric subunit as the cofactors. A general scheme of L-arginine oxidation is given below:⁶



The oxidation occurs stereospecifically, L-arginine (but not its D-isomer) is the only source of nitric oxide.¹¹ L-N-Hydroxyarginine (**1**) is an intermediate product of L-arginine oxidation.^{12–20} Compound **1** was synthesised¹³ from the α,ω -diamino acid ester (**2**) *via* the N-cyano derivative, which was further converted into

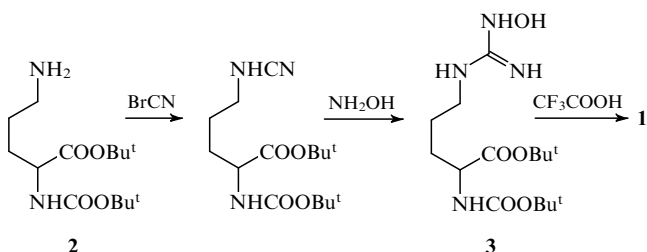
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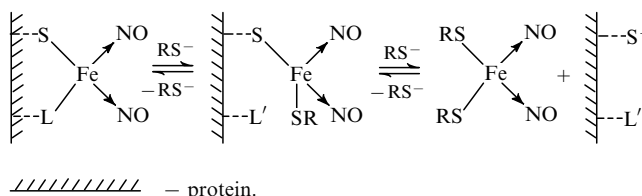
the *N*-hydroxyguanidine intermediate (**3**). Deprotection of the carboxyl and α -amino groups resulted in *N*-hydroxyarginine **1**.



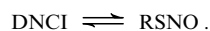
Like L-arginine, *N*-hydroxyarginine **1** causes the relaxation of vessels, which can be prevented by the NO-synthase inhibitors, *N*^ω-methyl- and *N*^ω-nitroarginines.¹³ These data agree well with the finding that *N*-hydroxyarginine **1** is the intermediate in the syntheses of NO and L-citrulline (L-Cit) from L-arginine.¹³ Special experiments^{16,17} have shown that L-arginine oxidation by NO-synthase occurs in at least two stages. At the first stage, which requires the presence of NADPH and oxygen, *N*-hydroxyarginine **1** is formed; the second stage, which requires B-H₄, oxygen, and 0.5 equiv. of NADPH, gives L-citrulline and nitric oxide. The same authors have established that *N*-hydroxyarginine **1** is a good substrate for inducible NO-synthase (i-NO-S). It is necessary to note that the oxidation of *N*-hydroxyarginine **1** with a labelled ¹⁵NOH-group results in ¹⁵NO₂⁻ and ¹⁵NO₃⁻ (the products of NO transformation), whereas the compound with a labelled ¹⁵NH-group of the imidoxime fragment gives nonlabelled NO₂⁻ and NO₃⁻ anions. Consequently, i-NO-S utilises only the *N*-hydroxylated fragment for its oxidation. Using H₂¹⁸O, it has been shown that L-citrulline formed upon the oxidation contains no label, *i.e.*, it is formed with the participation of O₂ rather than water. The idea that *N*-hydroxyarginine **1** is the intermediate in NO biosynthesis *in vivo* is in good accord with data on the pharmacological activity of this compound in comparison with the activity of arginine (including the experiments with NO-S inhibitors).¹⁸ There is evidence²⁰ of the ability of compound **1** to undergo oxidation in cells to nitric oxide and nitrites also in the absence of NO-S, apparently *via* catalysis mediated by cytochrome P-450. Nevertheless, the main pathway of nitric oxide formation in the organism is the NO-S-catalysed oxidation of L-arginine. Two major isoforms of NO-S have been described in the literature, namely, the constitutive NO-synthase (c-NO-S) found in vascular endothelium and brain and inducible NO-synthase (i-NO-S) present in activated macrophages. The constitutive isoform requires Ca²⁺/calmodulin for its activation and can be subclassified into endothelial and neuronal isoforms. The former generates NO that influences the lowering of arterial pressure and inhibits the aggregation of platelets; the latter (the neuronal enzyme) functions as a neurotransmitter. The main function of i-NO-S is the immune protection of the organism, *i.e.*, the synthesis of NO, a cytotoxic and antiinflammatory agent. Unlike c-NO-S, i-NO-S does not require regulation by Ca²⁺ (see Refs 10, 21).

Of great importance is the further fate of nitric oxide in living organisms, namely, its involvement in various biochemical processes and the mode of its deposition in cells. Although in many studies the role of a vasodilating agent has been ascribed to nitric oxide, the identity of NO with the so-called endothelium-derived relaxation factor (EDRF) is very doubtful due to the high reactivity of nitric oxide and, correspondingly, the high probability of its rapid biotransformation in living organisms. The fact that, unlike EDRF and *S*-nitrosothiols, NO enters into reaction with hemoglobin (Hb) to give a HbNO complex (data from the tracer technique, EPR spectroscopy), allowed one to conclude that EDRF is not free nitric oxide but rather is an *S*-nitrosothio compound of the *S*-nitrosocysteine type.²² *S*-Nitrosothiols have been proposed as candidates for EDRF in a number of other investigations.^{2,23–25} However, there exists an alternative view-

point,^{26–31} according to which EDRF is represented by dinitrosyl complexes of non-heme iron (DNCI) with low-molecular-weight thiol ligands. Both types of compounds (nitrosothiols and DNCI) have been detected in cells and tissues that generate nitric oxide from L-arginine under catalysis by NO-S.^{29,30} The same authors have demonstrated that these compounds can undergo interconversions, *i.e.*, the deposition of nitric oxide according to both these mechanisms is not mutually exclusive. Protein ligands seem to have greater affinity for Fe(NO)-groups; however, in the interaction with thiols, such as cysteine and acetylcysteine, the following equilibrium is established:²⁹



According to Vanin *et al.*,²⁹ protein DNCI provide stable storage of nitric oxide, whereas low-molecular-weight DNCI act as carriers. In endothelial cells, EDRF is largely represented by DNCI, whereas in the intercellular medium, by *S*-nitrosocysteine.³⁰ Since DNCI are much more stable than *S*-nitrosothiols, in animal organisms the equilibrium is markedly shifted to the left and the viewpoint, according to which EDRF is predominantly represented by iron complexes, appears to be rather convincing.³¹

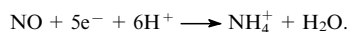


The binding of nitric oxide by iron seems to determine also the activation of soluble guanylate cyclase (SGC) responsible for GTP transformation into cGMP and the biochemical and biological effects produced thereby. It has been found³² that the UV spectrum of SGC changes under the influence of NO. Simulation of this system has revealed that after addition of nitric oxide protoheme-CO complexes transform into the pentacoordinated Fe(II)-NO complexes that apparently mimic the behaviour of SGC. It is assumed³³ that NO nitrosylates heme-SGC to give a nitrosyl-heme complex, in which iron is out of the plane of the porphyrin ring. The structure of the complex becomes similar to that of the SGC activator, protoporphyrin IX, and SGC activation takes place. The NO influence on SGC having been established, the activation of this enzyme by several nitric oxide complexes with transition metals has been studied.³⁴ Three types of nitroso complexes have been examined: sodium nitroprusside, Na₂[FeNO⁺(CN)₅], in which the NO group bears a positive charge (nitrosonium cation), K₃[CrNO(CN)₅] and [CoN(O)(NH₃)₅]SO₄ (where NO is the neutral group), and K₃[CoN(O⁻(CN)₅], where NO is coordinated as the anion. The most effective activator of SGC is sodium nitroprusside whose activating effect is determined by the interaction of NO⁺ with the heme of the enzyme. Nitroso complexes with cobalt and chromium, in which NO is a neutral group, activate SGC insignificantly, whereas the complexes with the NO⁻ anion inhibit the enzyme. In contrast to nitroprusside, other nitroso complexes have no hypotensive effect mediated by a heme-dependent mechanism.

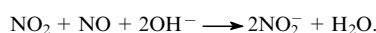
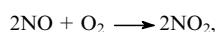
Before we come to the consideration of the material concerning the analysis of various types of structures that are responsible for the release of exogenous nitric oxide or inhibit its formation in living organisms, it seems expedient to consider in this section the analytical methods allowing the identification of NO.

The main techniques (chemiluminescent, electrochemical, EPR, spectrophotometrical, chromatographic, electrophoretic, and fluorimetric) used to determine nitric oxide have been described in detail in a recent review.⁸ Here it seems appropriate to cite some papers not mentioned in this review. Thus NO has been determined colorimetrically as nitrite anion and by EPR spectroscopy as the nitrosyl-ferrohemoglobin paramagnetic

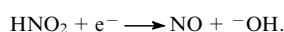
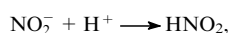
complex obtained by decomposition of thionitrites in the presence of oxyhemoglobin.³⁵ Analysis of NO has been performed by EPR spectroscopy of an iron–mononitrosyl–dithiocarbamate complex.^{15, 28, 36} A chemiluminescent method has also been used.^{37, 40} Special reference should be made to an indirect electrochemical method recently developed for the determination of nitric oxide.^{41–45} It turned out that NO can be identified polarographically, since it is reduced on a mercury dropping electrode (MDE) in acidic media (pH < 3) to give an irreversible five-electron wave.⁴¹



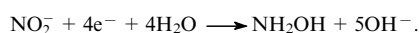
The wave appears at -0.77 V (relative to SCE, saturated calomel electrode) and rapidly disappears when nitrogen is passed through. This does not allow one to consider this method as an analytically applicable one. It is more appropriate to detect NO from the reduction current of NO_2 that is formed upon the interaction of NO with dissolved atmospheric oxygen. In this case, the determination is carried out at a pH close to the physiological one.



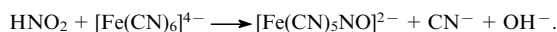
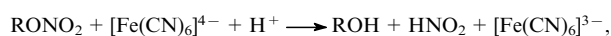
In weakly acidic solutions (pH 3–4) a non-dissociated HNO_2 is formed, which is discharged on the MDE via a one-electron mechanism ($E_{1/2} = -1.0$ V vs SCE).



The appearance of this wave is an indirect marker of the presence and concentration of NO in the solution. Yet, another possible method for the determination of nitric oxide is the introduction into the solution of polyvalent cations (La^{3+} , Ce^{3+} , and Nd^{3+}).⁴¹ In this case, a wave with $E_{1/2} = -1.2$ V is observed.



To further improve this method, a polarographic procedure^{42–45} has been developed for the determination of NO in the form of the nitroprusside anion, which is formed upon the reduction of the compound under study with potassium ferrocyanide or upon its oxidation with potassium ferricyanide. For example, in the reaction of well-known NO generators, such as nitrites, with the ferrocyanide anion the following processes take place:



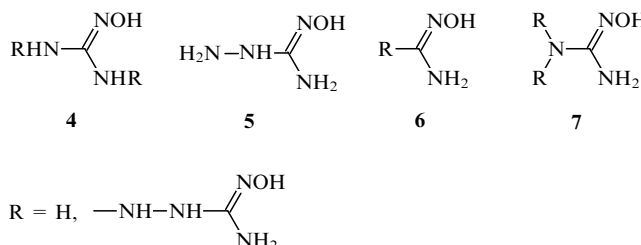
This interaction gives a polarographically active nitroprusside anion, and, in the appropriate selection of optimum conditions, this process can be used for reliable quantitation of nitric oxide.^{42–44} Another analytical procedure^{42, 45} is based on a time-dependent decline of the anodic wave of cysteine in the presence of a nitric oxide source.

The data presented above point to the expediency of a search for compounds that can increase or decrease the nitric oxide content in organs and tissues, while the existence of reliable analytical methods for the determination of NO makes it possible to select the most promising NO donors *in vitro*. Below we consider methods of synthesis of NO donors and provide ample data on nitric oxide generators and inhibitors of its NO-S-catalysed *in vivo* synthesis and discuss some biological and toxicological problems arising from the effect of exogenous compounds on various biological systems.

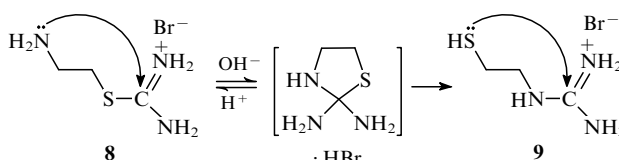
III. Exogenous donors of nitric oxide

1. Guanidines and related compounds

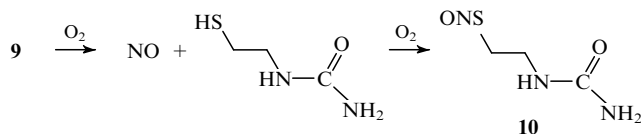
As indicated above, it is the guanidine fragment of L-arginine, the target for NO-S, that undergoes oxidation to the *N*-hydroxy derivative **1** and further to citrulline and nitric oxide. It is supposed that the binding of substrates with NO-S occurs also *via* the amino-acid part, but largely it is due to the guanidine fragment (with the heme of the enzyme and a special site of ‘guanidine binding’).⁶ It could therefore be expected that some compounds having guanidine or guanidine-like groups can act as substrates for NO-S and can be transformed *via* the oxidative NO-synthase mechanism (including NO-S catalysis) with the evolution of NO. First of all, this applies to the main endogenous substrate, L-arginine, since enzymic processes are mostly highly specific. Of the investigations concerning arginine itself, special mention should be made of a study that has demonstrated that this amino acid and the ethyl ester of *N*^ω-benzoyl-L-arginine can lower intra-ocular pressure *in vivo*.⁴⁶ In addition, L-arginine and its derivatives with lipophilic substituents can be used in the treatment of ischemia retinae.⁴⁷ The authors of these two papers believe that these phenomena are due to the ability of L-arginine and its derivatives to undergo oxidation with the liberation of nitric oxide and, correspondingly, cause the relaxation of blood vessels resulting in the lowering of blood pressure. The vasodilating effect of *N*-hydroxyarginine **1** is enhanced during its interaction with nitric oxide. It was shown that the reaction of compound **1** with NO, HNO_2 , and other nitrosating agents gives an adduct able to cause the relaxation of vessels.¹⁹ The reaction of certain cyanamides, carbodiimides, and other compounds with hydroxylamine resulted in a series of the corresponding *N*-hydroxyguanidines **4–7**.¹⁹ These compounds also give adducts with nitrosating agents that liberate nitric oxide in aqueous solutions (data from chemiluminescent analysis).¹⁹



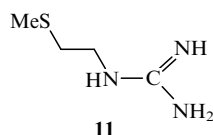
The structure of these adducts has not been established; however, it has been shown that they are stable prior to dissolution. In aqueous solutions, they decompose at different rates, the decomposition being irreversible at low pH (1.0–1.5). In organic solvents, the degradation occurs rapidly but the yield of NO is small. Using labelled nitrosating agents, it has been demonstrated that ^{15}NO incorporates into the adduct and it is this nitrogen (^{15}N) that is lost upon decomposition. Pharmacological tests have revealed the relaxation of vessels under the influence of these compounds. In this case, more labile adducts give a short-term and sharp relaxation, whereas slowly decomposing adducts elicit a more prolonged (on a time scale) response of lower intensity. It is self-evident that apart from the NO formed by degradation of its adducts with hydroxyarginine **1** and some other hydroxyguanidines, the NO formed by the oxidation of the guanidine fragment of arginine is also released. The β -aminoethylisothiuronium salt **8**, which readily rearranges into β -mercaptoethylguanidine **9** at pH 7.0, has been studied.^{48, 49}



The equilibrium ratio **8**:**9** has been quantitatively estimated by the polarographic method.⁴⁹ It has been found that the amine **8** is completely converted into the thiol **9** at pH 7.0. This finding has led the authors to assume the probability of the same transition *in vivo*. It was conjectured that the oxidation of **9** with the formation of NO is accompanied by the capture of NO by the thiol group to give the *S*-nitrosothiol **10**, and thus the deposition of the released nitric oxide takes place.

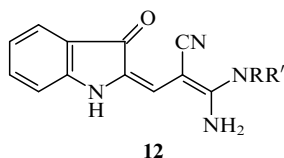


To test this hypothesis, β -methylthioethylguanidine **11** has been synthesised.



It turned out that the guanidine **11** activates SGC far less efficiently than thiol **9** and produces a less pronounced hypotensive effect, which probably confirms the expediency for a search for systems containing 'traps' capable of retaining and preserving nitric oxide for some time along with fragments responsible for NO release. This question will further be discussed in the consideration of other NO generators. It is worth special note that the oxidation of the thiol **9** seems to occur *via* the same mechanism as that of L-arginine, *i.e.*, with the participation of NO-S. Evidence in favour of this conclusion can be derived from the fact that SGC is not activated when the thiol **9** is used in combination with the NO-S inhibitor, *N*^ω-methylarginine.

Yet, another new type of NO-donor is represented by dienediamines of the indolinone series **12**.^{50, 51}

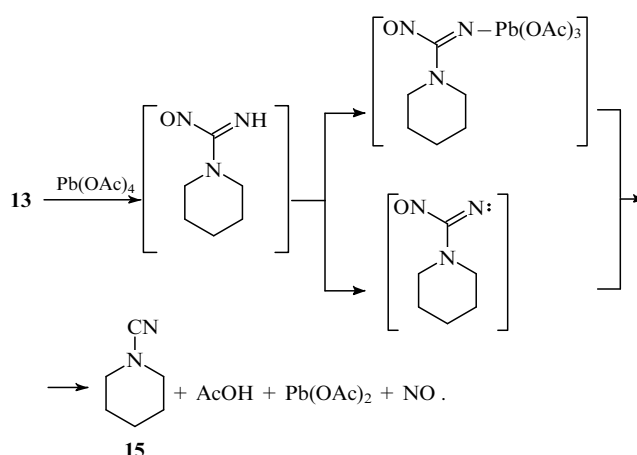


Compounds **12** form nitric oxide upon oxidation and, depending on the substituent at the nitrogen atom, manifest a more or less pronounced ability to activate SGC and exert hypotensive activity *in vivo*.

The chemical oxidation of *N*-hydroxyguanidines, such as **1**, **13**, and **14**, which is accompanied by NO release, has been studied.¹⁵ Of the oxidants tested only two, *viz.*, lead tetraacetate and potassium ferricyanide/hydrogen peroxide, have been found to direct the process along the desired pathway.



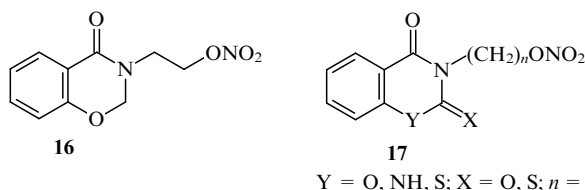
N-Cyanopiperidine **15** has been isolated and identified as one of the oxidation products of compound **13**. A scheme of the process that differs basically from the enzymic oxidation of L-arginine and *N*-hydroxyarginine has been proposed:¹⁵



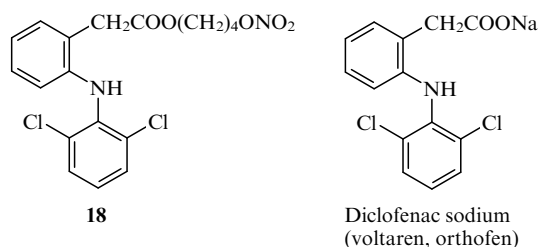
Interestingly, chemical oxidation does not result in ureas, *i.e.*, products similar to citrulline formed upon arginine oxidation. This fact provides additional evidence in favour of the enzymic pathway of the *in vivo* oxidation of guanidine derivatives. It is noteworthy that oxidation by other reagents results in HNO which dimerises to give HON=NOH. The decomposition of the latter gives N₂O and H₂O.

2. Nitrates

For the derivatives containing the guanidine or modified guanidine fragment, oxidation is the main pathway of NO generation. On the contrary, the formation of nitric oxide from nitrate vasodilators (drugs of the nitroglycerin type that have been used for many years) and related compounds requires reduction. It is now obvious that the coronarodilator effect of nitrates is associated with enhanced release of nitric oxide by these donors.^{37, 38, 52–58} Nitrates are traditionally used in the treatment of stenocardia but their clinical applications can further be extended to diabetes mellitus, atherosclerosis, and vasospasm. In addition to the well-known nitrates,^{37, 38, 52} some authors offer novel compounds, such as nitroxyalkyl coumarins.⁵³ The activity of some representatives of this series exceeds that of nitroglycerin 2- to 10-fold. A recent report⁵⁴ on a novel drug, the benzoxazine derivative **16**, points to an improved action on coronary vessels. This drug is undergoing the second stage of clinical trials. Some novel oxazine, thiazine, and pyrimidine derivatives **17** manifest antiischemic activity.⁵⁴

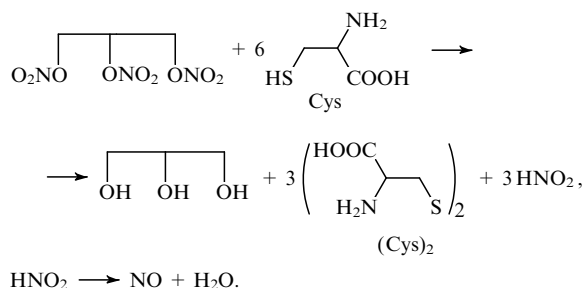


Data have been given⁵⁵ on the vasodilating and antiaggregating activity of NO donors, such as *S*- and *N*-nitroso compounds, relative to nitroglycerin. The vasodilating action of nitroglycerin is at a sufficiently high level; however, with regard to the inhibition of platelet aggregation this drug is strongly inferior to *S*- and *N*-nitroso compounds. Nitrofenac (diclofenac δ -nitroxybutyl ester, **18**)⁵⁷ belongs to novel NO donor compounds.



With regard to antiinflammatory and antipyretic action, nitrofenac is similar to diclofenac sodium (voltaren, orthofen) but its antithrombotic activity (which is characteristic of NO donors) is much higher. However, the main advantage of **18** in comparison with diclofenac sodium is its ability to markedly reduce gastrototoxicity without any detriment to its ability to inhibit prostaglandin synthesis. This important property is ascribed to the presence of a nitrate fragment in compound **18**.

Direct evidence in favour of NO formation from nitrates in the presence of thiols has been obtained using the polarographic method.⁴⁵ The course of the reaction of nitroglycerin with thiols was followed by the decline of the anodic waves of thiol and nitrate. Thus, the polarographic wave reflecting cysteine oxidation gradually declines with time according to the equation:

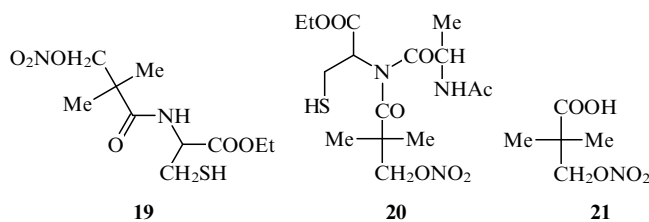


It has been established that nitroglycerin reduction with cysteine or unithiol (sodium 2,3-dimercaptopropane sulfonate) occurs in two steps, *i.e.*, reductive hydrolysis of the nitrate with thiol and reduction of the NO₂⁻ formed to NO. Disproportionation of HNO₂ is also possible:

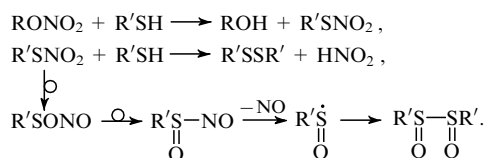


The rate of the nitroglycerin reaction with thiols is rather low, being essentially less than the manifestation of the therapeutic effect of this drug, which suggests the enzymic formation of nitric oxide from nitroglycerin *in vivo*.⁴⁵ One of the most important problems in the clinical application of nitrates is the development of a tolerance effect, which is believed to be associated with different mechanisms of blockade or metabolism of nitroglycerin and/or with the effect of its active metabolite, nitric oxide.⁵⁸ In this case tolerance is not eliminated with an increase in the nitroglycerin dose. A proposal has been put forward⁵⁹ that tolerance is caused by rapid depletion of intracellular depots of cysteine or, in more general terms, by the deficiency of SH-containing compounds. This hypothesis has given rise to a noticeable trend in the synthesis of SH-containing NO donors. In this case 'intramolecular assistance' is possible (as in the case of β-mercaptoethylguanidine) consisting in intramolecular trapping of the released NO to give rather unstable S-nitrosothiols, which serve as a source of NO in the organism. Synthetic compounds based on this principle are highly effective vasodilators, potent nitric oxide donors, and SGC activators. Among them, compound **19** exerts the highest activity.⁵⁹

Apparently, compound **19** and its analogues do not produce the effect of development of tolerance. Synthesis of the ethyl ester of [N-(3-nitroxypivaloyl)-N-(N'-acetyl-DL-alanyl)-L-cysteine (SPM-5185, **20**), a coronarodilator drug comparable in activity with nitroglycerol, has been described.⁶⁰⁻⁶³



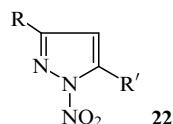
To check the idea that the presence of a thiol group in the molecule of nitrate is necessary to exclude the development of tolerance, a comparative study of the biological effects of compounds **20** and **21** has been carried out. It has turned out that the activity of the former markedly exceeded that of the latter, which was devoid of the thiol group; however, neither of these compounds induces any noticeable tolerance. This finding made it possible to assume⁶¹ that the cysteine fragment of compound **20** is not necessary and the reduction of the number of thiol groups can hardly be the reason for tolerance. The fact that tolerance did not develop with ester **20** has been specially examined and confirmed.⁶⁴ However, in another recent study⁶⁵ it has been demonstrated again that it is particularly the depletion of thiol groups that is the true reason for the development of tolerance to nitrates. Bron *et al.*⁶⁵ have synthesised compounds containing ONO₂⁻ groups together with a thiazolidine fragment whose hydrolysis gives free thiol compounds. Pharmacological studies of these compounds have made it possible to conclude that the presence of the released nitric oxide together with the liberated thiol groups in the system prevents nitrate tolerance. In conclusion, let us return to the reaction of nitrates with thiols which, as can be evidenced from the above data, is the most important mechanism of their biological action. The reaction of thiols with nitrates has been analysed⁹ and it has been established that the thiol structure is the crucial factor. All thiols decompose nitrates to the nitrite anion, but only some of them (cysteine, N-acetylcysteine) convert them into nitric oxide. If NO is formed (even together with NO₂⁻), the activation of SGC occurs; if only NO₂⁻ is formed, no activation of SGC takes place. These differences in the behaviour of thiols were rationalised in terms of a possible intramolecular rearrangement (thionitrate → sulphenyl nitrite).



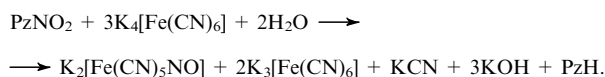
Obviously, the validity of the concepts concerning nitrate metabolism needs further verification and analysis.

3. Other nitro-, nitroso-, and related compounds

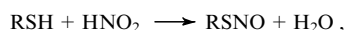
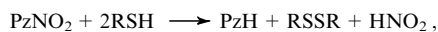
Like O-nitro, N-nitro derivatives can also be generators of nitric oxide, which can be exemplified by the study of nitropyrroles (PzNO₂, **22**).⁶⁶



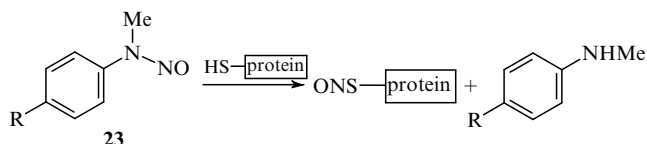
Both electrochemical and chemical reduction of these compounds with potassium ferrocyanide or cysteine gives nitric oxide. Compounds **22** activate SGC. The putative mechanism of this transformation is given below, using the reaction with potassium ferrocyanide as an example:



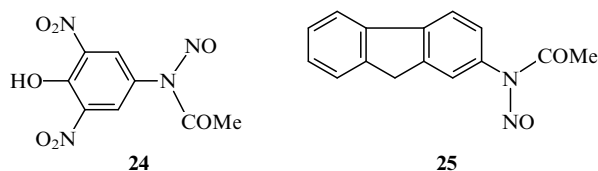
With thiol compounds (cysteine), pyrazoles **22** react according to the scheme:



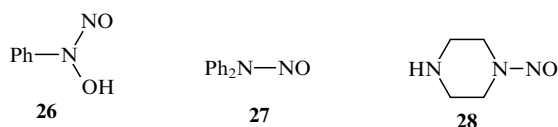
A number of investigations have been dedicated to the analysis of compounds containing an *N*-nitroso group. A series of *N*-methyl-*N*-nitrosoanilines **23**, which, as it turned out, were able to *S*-nitrosate cysteine-containing compounds (*e.g.*, papain) and thus form stable NO-depots, have been investigated.⁶⁷



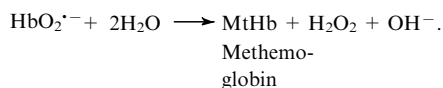
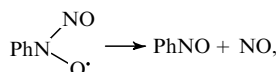
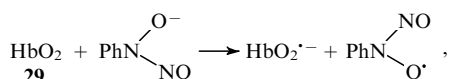
N-Nitroso compounds **24** and **25**, which exhibit a pronounced mutagenic effect, manifest vasodilating properties; the vascular response can be prevented by hemoglobin that binds NO or by Methylene Blue that inhibits guanylate cyclase.⁶⁸



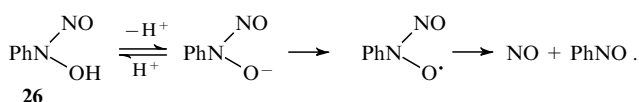
Interestingly, compounds **24** and **25** can deaminate DNA bases. It is assumed⁶⁸ that the above effects are due to the release of nitric oxide. A group of *N*-nitroso compounds **26**–**28** acting as nitric oxide donors have been studied.³⁶



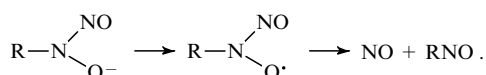
For *N*-nitroso-*N*-hydroxylaniline **26**, an oxidation reaction with involvement of oxyhemoglobin **29** has been suggested.



The scheme of oxidation of compound **26** without the involvement of hemoglobin is given below:⁶⁹



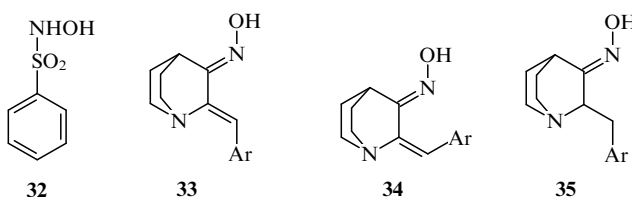
For compounds of the type **26**, a peroxidase-catalysed enzymic oxidation is observed. The oxidation can also be modelled electrochemically.⁷⁰



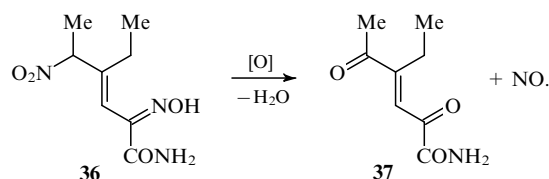
In both cases nitric oxide is formed.

Some studies have dealt with the analysis of derivatives of *N*-nitroso-*N*-alkoxy compounds.^{69–71} Thus compounds $\text{RN}(\text{NO})\text{OR}'$ (**30**: $\text{R} = \text{R}' = \text{Me}$; **31**: $\text{R} = \text{R}' = \text{Et}$) can effectively generate nitric oxide, which may be the reason for their far greater cancerogenic activity⁷¹ in comparison with, *e.g.*, *N*-nitrosodimethylamine.

These studies are close to those on the oxidation of compounds with the N–O bond.^{72–76} This group includes nitrones giving nitric oxide upon photolysis⁷³ and activating SGC, nitroxyl (HNO) producing biological effects similar to those of NO,⁷⁴ peroxynitrite (ONOO^-), which gives NO upon interaction with glucose and causes the relaxation of vessels inhibited by oxyhemoglobin,⁷⁵ and *N*-hydroxybenzenesulfamide **32**,⁷⁶ Piloti's acid, which upon oxidation releases NO (presumably this process occurs *via* an enzymic route).⁷⁶ Oximes (*e.g.*, **33**–**35** derived from quinuclidone-3) have turned out to be interesting objects for the study of nitric oxide generation.



Using an indirect electrochemical method [$\text{K}_3\text{Fe}(\text{CN})_6$ and $\text{K}_4\text{Fe}(\text{CN})_6$, see above], it has been established that the majority of these compounds generate NO upon oxidation.^{44, 77} The highest yield of nitric oxide has been observed for compounds **34** and **35** (in both cases, Ar is *o*-hydroxyphenyl); *i.e.*, the proximity of the oxime fragment and the phenolic hydroxyl favours the formation of NO. It is essential that these compounds are oxidised to NO even by atmospheric oxygen. These oximes activate SGC and have hypotensive action. A conclusion has been made⁴⁴ about the possible role of the phenolic *ortho*-hydroxyl group as nitric oxide carrier, which stabilises NO in the form of *O*-nitrites or *O*-nitrates. The interaction of NO with phenolic antioxidants and phenoxyl radicals that can be regarded as nitric oxide carriers in biological systems is documented.⁷⁸ The oxidation of compound **36** containing both the oxime fragment and the nitro group has been studied.⁷⁹



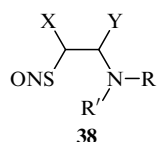
At pH 7.5, compound **36** rapidly transforms into the diketone (**37**) with the release of NO. The latter has been identified by EPR spectroscopy, colorimetric titration, and using a procedure based on the interaction with the tyrosyl residue of ribonucleotide reductase. Compound **36** is a potent vasodilating agent, it activates SGC and increases the level of intracellular cGMP. This study provides no direct data as to which of the groups (nitro group, oxime group, or both) make the main contribution to NO production.

There is experimental evidence that 5-nitrofurans and 5-nitroimidazoles form nitrosyl complexes of hemoglobin in the presence of ascorbic acid as reducing agent, *i.e.*, they released nitric oxide.⁸⁰ In conclusion, it is appropriate to mention that NO is formed in the photolysis of 2-methyl-2-nitrosopropane.⁸¹ Upon irradiation, this compound induces the relaxation of vessels, activates SGC, and, correspondingly, increases the cGMP level in biological solutions.

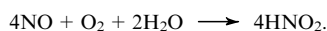
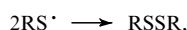
4. S-Nitrosothiols

Since *S*-nitrosothiols represent, perhaps, the most abundant and especially well-studied group of exogenous generators of nitric

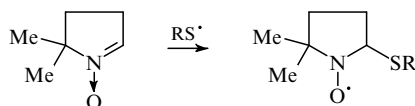
oxide, it seems expedient to isolate them as a separate class of NO donors. Roy *et al.*³⁵ have proposed the main requirements for nitric oxide generators that confirm the expediency of a search for new drugs particularly in the *S*-nitrosothiol series. The reasons for this are: (i) simplicity of synthesis and the possibility of isolation of pure compounds in a stable (predominantly solid) form and (ii) capability for relatively fast degradation in aqueous solutions at physiological pH resulting in the release of NO without any redox activation. This decomposition occurs with quantitative liberation of NO and is not accompanied by the formation of toxic side products. A large group of *S*-nitroso compounds of the general formula **38** have been synthesised.³⁵



The stability of these compounds in solution has been studied, and their ability to generate nitric oxide was confirmed by several known methods. Quantitative determination of the half-life of *S*-nitrosothiols **38** in a phosphate buffer at pH 7.0 has been carried out: they vary from several minutes to tens of hours depending on the structure. It is believed that the formation of NO is based on homolytic cleavage of the S–N bond.



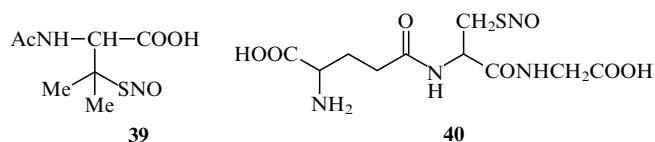
The production of NO is accompanied by the formation of the RS[•] radical, which is so unstable that it cannot be detected by EPR spectroscopy. If 5,5-dimethylpyrroline *N*-oxide is used as a trap, its reaction with the thiyl radicals yields stable paramagnetic species that can be detected by EPR spectroscopy.³⁵



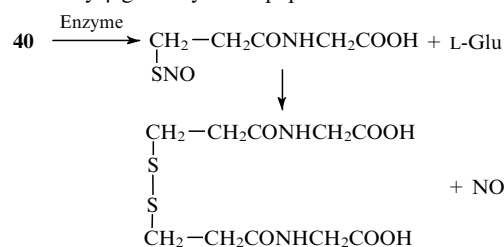
The effect of structure on the stability of nitrosothiols has been ascribed to the contribution of the resonance structure **A** stabilising the molecule with respect to the homolytic cleavage of the S–N bond. The contribution of this structure increases with an enhancement of the electron-donor properties of the radical R (in these cases the stability of *S*-nitrosothiols increases also).



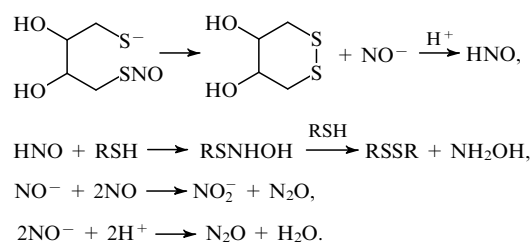
Thiyl radicals have been discussed by Feelish,⁹ who has demonstrated potential hazardous properties of these highly reactive compounds. They can not only undergo dimerisation, but also enter into other reactions, thereby giving compounds with unknown biological activity. Another potential danger from the use of *S*-nitrosothiols is the reaction of transnitrosation of SH groups of proteins. This reaction may cause irreversible modification of SH groups of enzymes and result in the formation of mixed disulfides with a partial or complete loss of enzymic activity. The problem of transnitrosation has been discussed in detail by Butler *et al.*,⁸² who have analysed the properties of *S*-nitroso-*N*-acetylpenicillamine **39** and *S*-nitrosoglutathione **40**.



Compounds **39** and **40** differ essentially in their chemical properties. The former is unstable; its decomposition to the corresponding disulfide and NO is catalysed by Cu²⁺. The latter is stable in solutions over many hours and are not affected by copper cations. Dicks⁸³ has pointed to the long induction period preceding the decomposition of compound **40** rather than its complete stability under these conditions. Nevertheless, *S*-nitrosoglutathione **40** is comparable in activity towards vascular relaxation with compound **39** and is more active as a platelet aggregation inhibitor. Compound **40** rapidly reacts with cysteine to give *S*-nitrosocysteine, an unstable compound, which rapidly generates nitric oxide.⁸² Thus, *S*-nitrosoglutathione **40**, which is relatively stable in solution, can produce NO at a high rate in the presence of cysteine. An alternative (and, seemingly, also fast) pathway of NO release from compound **40** is the enzymic pathway mediated by γ -glutamyl transpeptidase.

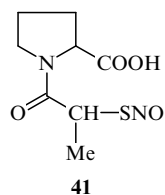


According to Park,⁸⁴ transnitrosation is the primary mechanism of the hypotensive effect of *S*-nitrosothiols. This viewpoint can be validated by the much lower rate of their hydrolysis relative to the development of the pharmacological effect. As for transnitrosation, it is a rather fast process. The same conclusion has been made by Mathews and Kerr.⁸⁵ Neuroprotective effects of *S*-nitrosothiols are caused by transnitrosation and, as stated by Arnelle and Stamler,⁸⁶ these processes occur with the participation of NMDA receptors (NMDA — *N*-methyl-D-asparagine). At the same time, neurodestructive effects of NO are probably due to its interaction with the superoxide anion (O₂^{•-}) resulting in peroxynitrite. It is conjectured⁸⁶ that the vasodilating, antiaggregating, and antimicrobial effects of *S*-nitrosothiols do not depend on the rate of NO release. Arnelle and Stamler⁸⁶ have considered the possibility of formation of such species as NO, NO⁺, and NO⁻. The amount of nitric oxide released from *S*-nitrosothiols has been determined by the rate of hemoglobin oxidation to methemoglobin. The high rate of transnitrosation has been attributed to the ability of nitrosothiols to act as NO⁺ donors, the rate of NO⁺ formation being higher than that of NO release. To study the NO⁻ release, the following model system has been used:



The fast formation of disulfides is accompanied by the release of hydroxylamine and N₂O, which is indicative of NO⁻ release. A conclusion is drawn from the experimental data that under physiological conditions *S*-nitrosothiols can act as NO⁺, NO, and NO⁻ donors. The authors advocate that the activity of these compounds is due not only to homolytic but also to heterolytic cleavage of the S–N bond. The papers dedicated to the synthesis of new, and analysis of the already known *S*-nitrosothiols are rather numerous.^{55, 87–92} Special mention should be made of the synthesis of *S*-nitrosocaptopril **41**.⁸⁸ This compound, which structurally represents a hybrid molecule, can influence both vital systems that maintain arterial pressure in living organisms

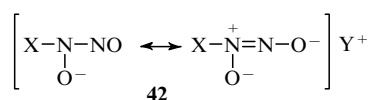
and can induce vasodilatation both through activation of SGC and inhibition of the angiotensin-converting enzyme (ACE).⁹³



Indeed, it has been shown experimentally that compound **41** possesses vasodilating properties and inhibits ACE and platelet aggregation. According to the authors, compound **41** can be used in the treatment of hypertension and various cardiovascular diseases; however, in our opinion, the clinical application of this compound is hardly possible because of its low stability.

5. NO Complexes with nucleophiles

One more group of compounds that can act as nitric oxide donors is represented by the so-called nonoates **42**, in which the ON–NO dimer is formally bound to the nucleophile through the nitrogen atom.^{94,95}

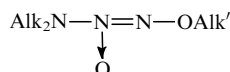


X = Et₂N, PrⁱNH;
Y = Na, NH₄, RR'NH₂.

These compounds are very stable as such, however, in solutions at pH 7.4 they are readily hydrolysed to give nitric oxide. In this case, like nitrosothiols, they do not require either reducing or oxidising agents for their hydrolysis. The rate of degradation is determined by the structure of the compounds and varies within a very broad range. Biological assays of this type of compounds have revealed that they are active vasodilating agents, platelet aggregation inhibitors, and regulators of cytochrome P-450 activity.^{39,96,97}

To localise the NO release in definite organs and tissues, the above system has been incorporated into a polymeric matrix. Various types of polymers have been synthesised, *e.g.*, by incorporation of Et₂N[N(O)NO][−]Na⁺ into polyethylene glycol, fusion of H₂NCH₂CH₂N[N(O)NO][−]CH₂CH₂NH₃⁺ with polycaprolactam, and polymerisation of H₂N(CH₂)₃N.[N(O)NO][−](CH₂)₃NH₃⁺ with dextran.³⁹ It has been established that the polymers containing the [N(O)NO][−] fragment and stored *in vivo* as localised sources of nitric oxide can slowly release NO at pH 7.0 and 30 °C. These polymers prevent platelet aggregation and inhibit cell proliferation *in vitro*.

Another pathway of NO release in the vicinity of a biological target is the creation of prodrugs incapable of releasing nitric oxide without preliminary metabolic transformation into the nonoate by enzymes specific for this particular cell target. To this end, the following alkyl derivatives have been synthesised:

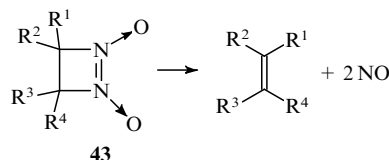


These compounds can release nitric oxide in solution and exhibit hypotensive activity *in vivo*.⁹⁸

6. Heterocyclic derivatives

a. 1,2-Diazete-1,2-dioxides

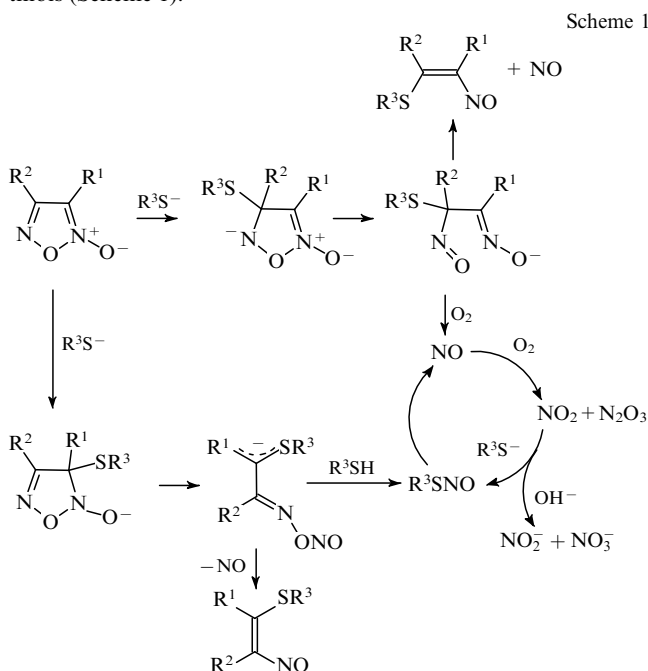
This class of compounds has been studied relatively recently.^{41,99,100} Compounds of the **43** type are known to decompose in aqueous solutions on moderate heating at physiological pH values to give nitric oxide. These data have been obtained using polarography⁴¹ and EPR spectroscopy.¹⁰⁰



Electrochemical studies of a series of 1,2-diazete-1,2-dioxides **43** have revealed that the rate of NO release depends on the structure of the radicals and varies within a rather broad range. Compounds **43** are potent activators of SGC, manifest a noticeable spasmolytic effect *in vitro*, and effectively lower arterial pressure *in vivo*. In all cases studied (rate of NO generation, SGC activation, as well as spasmolytic and antihypertensive effects) there was a convincing correlation between the experimentally determined series of activities. The rate of NO formation is the determining factor in the manifestation of the above biological effects. The highest activity was observed with compound **43** [R¹ = Br, R²–R³ = (CH₂)₄, R⁴ = Me] and the lowest activity, with compound **43** [R¹ = R⁴ = H, R²–R³ = (CH₂)₅].

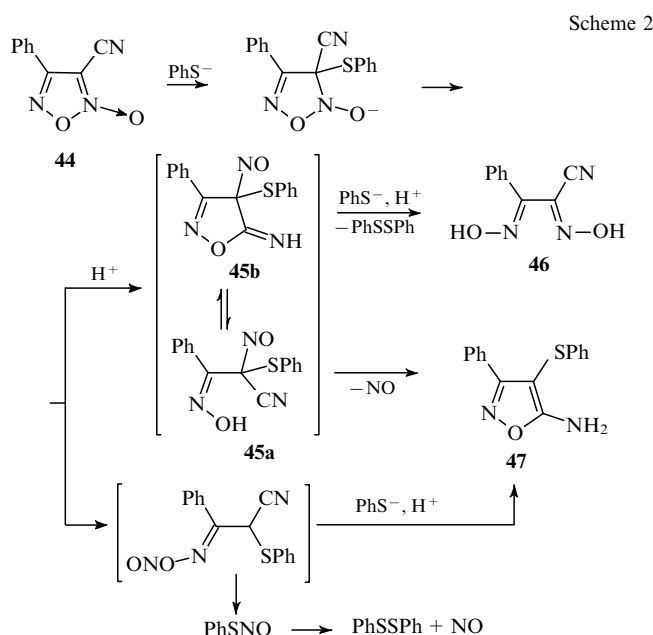
b. Furoxanes

A number of investigations have been dedicated to the study of the NO donor properties of furoxanes. It has been shown¹⁰¹ that the release of nitric oxide takes place in the reaction of furoxanes with thiols (Scheme 1).

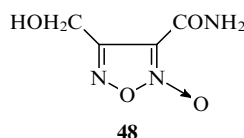


Furoxanes activate SGC and enhance the coronary blood flow. According to Feelisch *et al.*,¹⁰¹ furoxanes can be regarded as prodrugs that exert their action *via* the NO/cGMP pathway. The thiol-dependent release of nitric oxide from furoxanes has been studied in detail with the interaction of 4-phenyl-furoxane-3-carboxynitrile **44** with cysteine and thiophenol as an example. Compound **44** activates SGC, produces strong vasodilating action, and demonstrates high antiaggregating activity. The yield of NO₂ formed upon oxidation of NO in the presence of 5 mmoles of cysteine is 14±2% (after 1 min), 29±1% (after 5 min), and 40±2% (after 1 hour), and in the presence of 0.5 mmoles of thiophenol it is 64±2% within 1 hour. The reaction of **44** with thiophenol has been studied in detail¹⁰² and is summarised in Scheme 2.

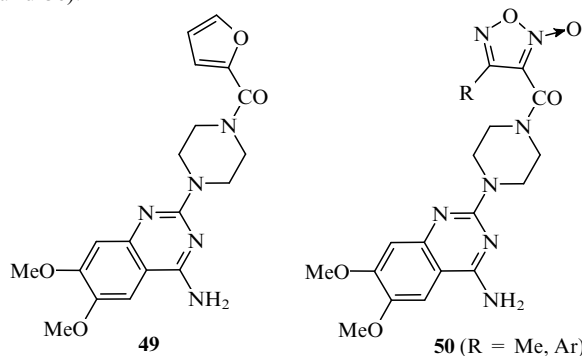
Compound **46** has been isolated in 20% yield, whereas isoxazole **47** formed from the intermediates **45a** ⇌ **45b**, in 60% yield. The experimental data provide an idea about the plausible



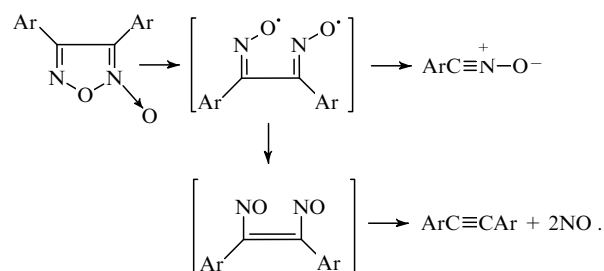
scheme of furoxane transformations leading to NO. A large series of biologically active furoxanes have been synthesised.^{103–105} No tolerance to 4-hydroxymethylfuroxane-3-carboxamide **48** has been noted.¹⁰⁴



In contrast with the above findings, Hecker *et al.*¹⁰⁵ have shown that the release of nitric oxide is not thiol-dependent. The lack of tolerance makes it possible to use furoxane derivatives in the treatment of cardiovascular diseases.¹⁰⁵ One more study¹⁰⁶ is dedicated to the synthesis of hybrid molecules, furoxane analogues of the known drug prazosin **49**, in which the furyl fragment has been substituted by the furoxanyl one (compound **50**).

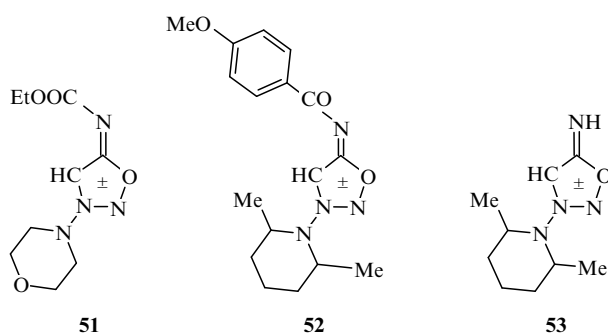


Compounds **50** act primarily as antagonists of α_1 -adreno-receptors. Although their action is weaker than that of prazosin. However, at higher concentrations the ability of these compounds to release NO also has a part in the vasodilating effect. And, finally, worth noting is the study,¹⁰⁷ in which the cleavage of the furoxane ring upon electron impact mass spectrometry has been studied. The proposed fragmentation rationalises the formation of nitric oxide:



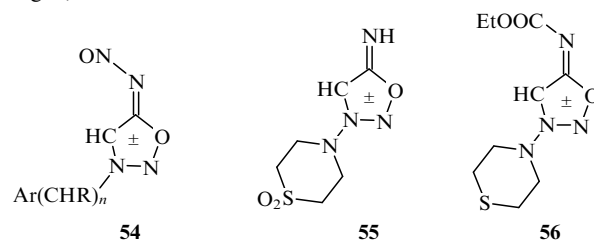
c. Sydnonimines

Another important class of heterocycles, for which the release of nitric oxide is characteristic under certain conditions, is represented by sydnonimines. Molsidomine **51**, one of the most potent antihypertensive drugs, belongs to this series.¹⁰⁸ Data on the high activity of this mesoionic heterocycle appear regularly in current literature (see, *e.g.*, Refs 55, 92, 109–113). Among compounds of this class, special mention should be made of the highly active nitric oxide donor, pirsidomine **52**, the biological activity of which is similar to that of isosorbide mononitrate, and the major metabolite of pirsidomine **53**.¹⁰⁹

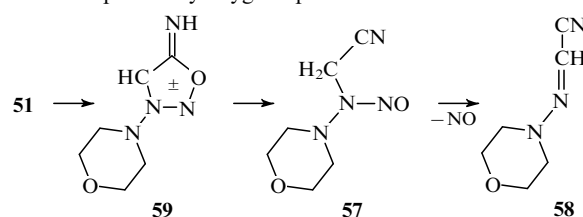


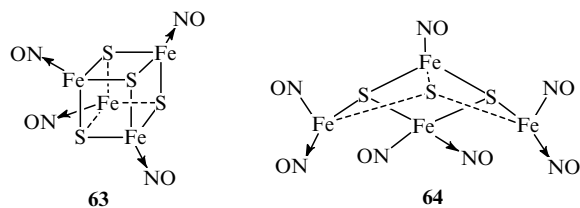
Unlike isosorbide mononitrate, compounds **52** and **53** do not induce tolerance, which is consistent with the hypothesis on the difference in the action mechanisms of sydnonimines and nitrates. In contrast to nitrates and, presumably, furoxanes, the generation of NO by sydnonimines does not require thiols.¹⁰⁹

The high antithrombotic activity has been observed for sydnonimines with different substituents, *viz.*, *N*-*exo*-nitroso derivatives **54**¹¹⁰ and compounds having thiazine residues at position 3 **55**, **56**.^{111,113} It is noteworthy that the activity of compound **56** is somewhat lower than that of its morpholine analogue, molsidomine **51**.¹¹³



It is stated¹¹² that sydnonimines are prodrugs and that their antianginal effects are due to the release of nitrogen oxide: the first stage of formation of type **57** metabolites from molsidomine occurs fast in neutral media. The formation of compound **58** and NO is accompanied by oxygen uptake.

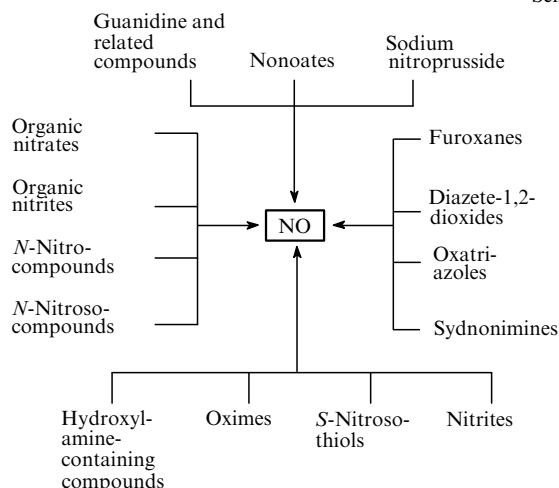




As expected, in the presence of oxyhemoglobin (the NO 'trap') or Methylene Blue (the SGC inhibitor) the biological activity of **63** and **64** drops drastically.

Most of the data presented herein concerning exogenous nitric oxide donors can be summarised in the Scheme 3.

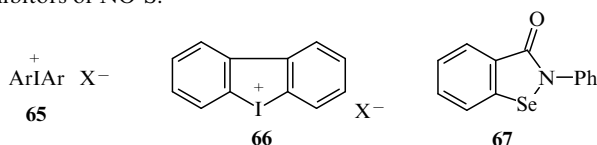
Scheme 3



This scheme illustrates the possibilities of control of the nitric oxide level in the organism through the introduction of NO generators having specific action mechanisms. Another approach to the regulation of the nitric oxide level in organs and tissues is the inhibition of NO-S responsible for NO production.

IV. Inhibitors of NO-synthase

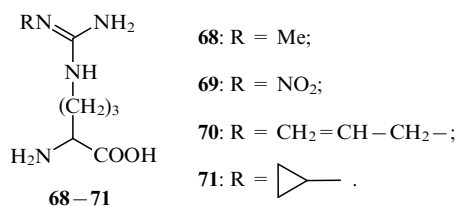
The foregoing sections dealt with the ways of the increasing the level of nitric oxide in organs and tissues under conditions of its insufficient production in living organisms. However, a number of pathological states, including cardiovascular diseases, infections, brain injuries, *etc.*, are accompanied by excessive release of NO. The undesirable toxicological effects of NO overproduction include extremal hypotension and/or cardiovascular collapse, cell injuries, and septic shock.¹⁰ Therefore, in some cases the necessity to inhibit NO-S has been mentioned. As above, the synthesis of nitric oxide is performed by NO-S isoforms.¹²⁴ Both c-NO-S and i-NO-S produce nitric oxide through the oxidation of the guanidine fragment of L-arginine by utilising molecular oxygen and NADPH as a cosubstrate. All the isoforms contain FAD, FMN, and heme iron as prosthetic groups and require BH₄ as a cofactor. Correspondingly, flavoprotein inhibitors can suppress the activity of NO-S. Thus the iodonium salts **65** and **66** and ebselenium (**67**), the selenium analogue of isothiazole, are potent inhibitors of NO-S.¹⁰



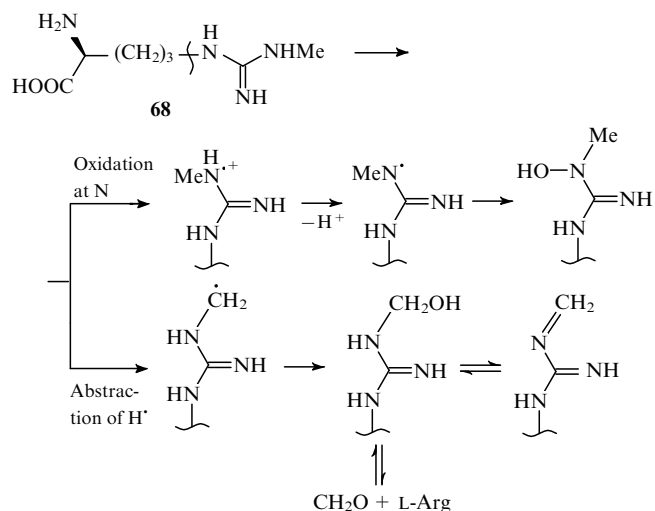
Ar = Ph, 2-thienyl

Arginine derivatives and related compounds are most commonly used as NO-S inhibitors. Since several reviews concerning approaches to the synthesis of NO-S inhibitors have been published recently,^{4,6,10} here we shall dwell only on some of the most

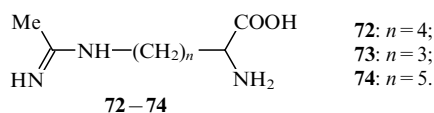
important and recent studies in this field. It should be mentioned, however, that the most important NO-S inhibitors are *N*^ω-methyl-**68** and *N*^ω-nitro-L-arginines **69**¹⁰ whose properties are still the subject of most intensive studies.^{125–129}



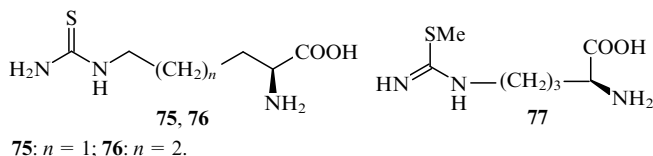
Thus compound **68**, the inhibitor of macrophage and i-NO-S, manifests its activity particularly through the alkylation of the enzyme.¹²⁵ It has been established that methylarginine **68**, similarly to aminoguanidine, inhibits NO-S and thus prevents the development of diabetic vascular functions.¹²⁶ Interestingly, methyl esters of the amino acids **68** and **69** manifest an analgesic effect that is ascribed to their influence on the central nervous system.¹²⁷ Inhibitors **68** and **69** potentiate the hypertensive effect of adrenaline.¹²⁸ Essentially, nitroarginine **69** induces strong arterial hypertension that can partly be prevented by administration of L-arginine, but not of D-arginine.¹²⁹ It was assumed¹³⁰ that compound **68**, being an irreversible inhibitor of macrophage i-NO-S, is subject to NO-S action according to the following two schemes:



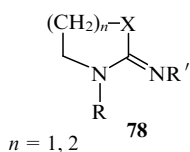
Olken and Marletta¹³¹ and Feldman¹³² have synthesised two novel i-NO-S inhibitors, *viz.*, *N*^ω-allyl- **70** and *N*^ω-cyclopropyl-L-arginines **71**. It is interesting that whereas the former is an irreversible inhibitor, the latter is reversible, *i.e.*, the effect of compound **70** is similar to that of nitroarginine **69**. The reasons for such a difference in the effect of compounds **70** and **71** are unclear. A series of structural analogues of arginine as NO-S inhibitors have been described.^{21, 133–135} Thus i-NO-S inhibitors (substituted arginines and homoarginines) have been used in the treatment of systemic hypotension caused by pathological 'overproduction' of nitric oxide.¹³⁴ As i-NO-S inhibitors, *N*⁶-(1-iminoethyl)-L-lysine **72**, *N*⁵-(1-iminoethyl)-L-ornithine **73**, and *N*⁶-(1-iminoethyl)-D,L-homolysine (**74**) have also been examined. It has been found²¹ that compound **72** is a strong selective inhibitor of i-NO-S, whereas the ornithine **73**, which is also an active inhibitor of i-NO-S, does not possess any selectivity and affects c-NO-S with equal strength.



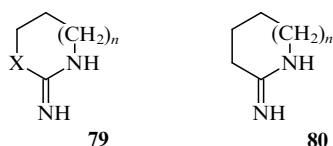
The synthesis of L-thiocitrulline **75**, L-homothiocitrulline **76**, and S-methylthiocitrulline **77** has been performed.¹³⁶ These analogues and derivatives of L-citrulline, the product of L-arginine oxidation in living organisms, are potent inhibitors of neuronal c-NO-S and i-NO-S. It is noteworthy that compound **77** is much more active in comparison with methylarginine **68**. The stereoselectivity of its interaction with the enzyme has been stressed again, and the activity of only L-enantiomers has been noted. D-isomers are fully devoid of the inhibitory activity.



Compounds **75** and **77** are potent pressor agents *in vivo*. The basic idea of the synthesis of this novel class of inhibitors was that the presence of a sulfur atom might result in their strong binding to the active centre of the enzyme in the vicinity of the heme iron, *i.e.*, this might enhance the interaction of the inhibitor with the enzyme. The experimental data seem to confirm this hypothesis.¹³⁶ One of the molecular fragments of arginine and related compounds responsible for the binding to NO-S is, undoubtedly, the guanidine moiety. Clearly, simple derivatives of guanidine and various amidines have also been tested as NO-S inhibitors.^{137–142} It has been shown that aminoguanidine is an NO-S inhibitor,^{126, 137} like N-arylguanidines¹³⁸ and cyclic guanidines or amidines of the general structure **78**.¹³⁹



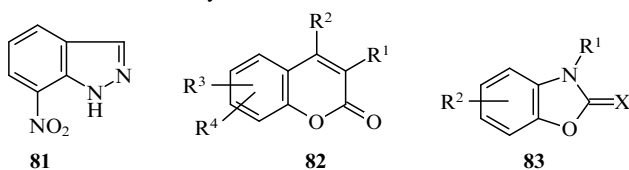
Compounds **78** preferentially inhibit i-NO-S.¹³⁹ Isothioureas and cyclic guanidines of the type **79**, cyclic amidines (**80**), and related compounds^{140–142} are active inhibitors of NO-S.



X = O, S, NH; $n = 0–4$.

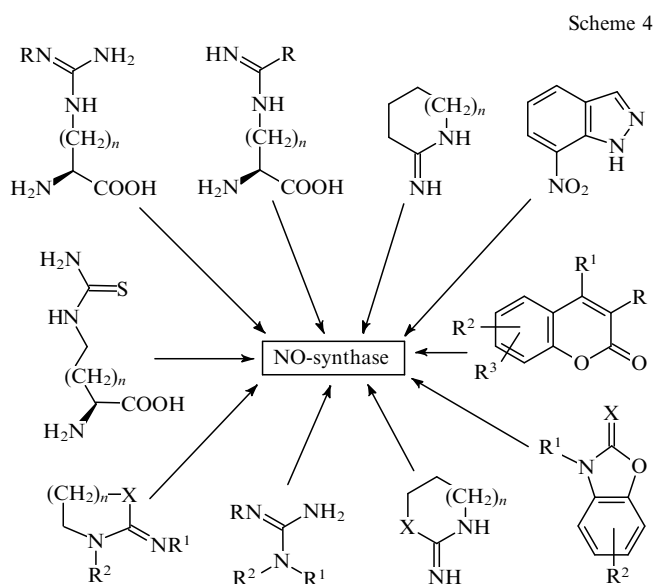
Some of the above-mentioned compounds can inhibit i-NO-S *in vivo*. Despite the great number of novel NO-S inhibitors having guanidine and amidine groups, the amino acid inhibitors **68**, **69**, and **73** are still most frequently used.^{143–146}

Novel inhibitors have been detected in the series of various heterocycles. They include 7-nitroindazole **81**,^{147–149} coumarin derivatives **82**,¹⁵⁰ and benzoxazole derivatives **83**.¹⁵¹ Compound **81**, possessing high analgesic activity, may be used as the 'starting material' in the elaboration of selective NO-S inhibitors acting on the CNS without any cardiovascular effect.



The data on inhibition of NO-S by compounds of various types considered in the above sections have been summarised in Scheme 4.

For the sake of completeness, it is necessary to stress once again that iron-heme-containing proteins and, correspondingly, heme-binding agents are inhibitors of NO-S. Thus carbon



monoxide is a good ligand for Fe^{2+} and a potent inhibitor of NO-S. Other heme-ligands of the cyanide type and even nitric oxide itself can play the role of inhibitors.^{10, 152}

V. Conclusion

Despite the fact that the enzymic formation of nitric oxide in vascular endothelial cells was discovered only in 1987, it follows from the above data that this biological mediator has aroused considerable interest among investigators, and the number of publications in this particular field of chemistry, biology, and medicine is steadily increasing. It can be emphasised once again that the present review deals primarily with the chemical and structural problems connected with the possibility of creating novel types of compounds able to generate or, contrariwise, inhibit NO production in the organism. Hence, a vast number of purely medical and biological problems, which are irrelevant to the subject of our discussion, have fallen outside the scope of this review. Also, the review gives relatively little information about such important problems as nitrate therapy; little attention is given to the well-known drug, sodium nitroprusside. Biological and clinical applications of the drug molsidomine have been described in less detail than they deserve. Problems of carcinogenicity and mutagenicity of N-nitroso compounds (*e.g.*, N-nitroso-N-methylurea and related compounds, such as N-methyl-N-nitroso-N'-nitroguanidine) have been described in only little detail. These problems have been considered in a number of the above-cited and other reviews^{1, 153–155} and the references cited therein.

In the contemplation of the above data, quite a large number of problems still remain unsolved, and even experimental data are often at variance with one another. This refers to differences in the pathways of chemical and enzymic oxidation of guanidine fragments; to the problems pertaining to the tolerance of nitrates that can be thiol-dependent or independent of the content of thiol compounds; to the demand for thiols upon NO release from furoxanes (for reference, see one of the most recent publications¹⁵⁶ in which it has been shown that some furoxanes can release NO in the absence of thiols, whereas for structurally related furoxane derivatives thiols are necessary); to the simultaneous release of nitric oxide and the superoxide anion; to the 'indirect' NO-generating effect of sodium nitroprusside, and so on.

Unquestionably, it is important to establish (although it is currently difficult to evaluate), to what extent the high reactivity of nitric oxide can influence some particular biochemical processes. For example, it has recently been established that NO oxidises dihydropyridines to pyridines.¹⁵⁷ When dihydropyridine

systems in the organism, such as NADH and NADPH, are considered, it is clear that this phenomenon needs special analysis.

After this review had been prepared for publication, a paper was published¹⁵⁸ that may have a great impact on the approach to problems related to NO formation from arginine and NO donors. It describes the discovery of 1*H*-[1,2,4]-oxadiazolo[4,3-*a*]quin-oxalinone-1 (SGC), which is the first direct inhibitor of NO-induced activation of SGC. The use of this compound presents indisputable interest, although it is still unclear what new avenues in the understanding of the role of NO it will open.

All these problems still await their solution. However, even now it can be predicted with certainty that the efforts aimed at creating novel generators of nitric oxide and specific inhibitors of NO-S isoforms hold much promise and represent a perspective trend in the search for novel effective drugs that has already turned out to be highly profitable in the theoretical sense. Further developments in this field may culminate in impressive achievements, including practical ones, even in the nearest future.

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Computer simulation of the structure and properties of non-crystalline oxides

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Abstract. The results of the studies of the structure and properties of non-crystalline (liquid and amorphous) oxide systems obtained using computer simulation methods are summarised. The models of simple oxides, homologous series of non-crystalline oxides and of binary and multi-component oxide systems are considered. The results of the simulation of the ion transfer are discussed. The ionic theory of oxides allows one to predict adequately the structural and thermodynamic properties of oxide systems except for the phosphate oxides and some other systems. The bibliography includes 222 references.

I. Introduction

Studies of the structure and properties of non-crystalline (liquid and amorphous) oxide systems obtained by powerful computer simulation methods, such as molecular dynamic (MD), static relaxation (SR), Monte Carlo (MC), and Reverse Monte Carlo are reviewed in this paper. General aspects of computer simulation have been discussed in detail in a number of reviews (see, for example, Refs 1–8) and will not be considered here. We confine ourselves to the analysis of specific applications of the above-mentioned methods to oxide systems.

The results of numerous experimental studies of oxide systems indicate a substantial contribution of ionic bonding to interatomic interactions. This is caused by the high electronegativity of the oxygen atoms. Nevertheless, the account of a covalent component is important in the simulation of structure and properties of the oxides. The covalent interaction is described in terms of three-particle potentials, which significantly increases the computational time required. Since ionic contribution cannot be neglected for oxide systems, the Coulomb interactions have to be considered as well. Construction of a model for an oxide with mixed ion and covalent bonding requires too many force parameters that are extremely difficult to calculate *ab initio*. Therefore, the models

have to be simplified. The choice of a model based only on the ionic interactions has significant advantages. Any doubts in the applicability of the ionic scheme were eliminated in a study, in which a purely ionic model of non-crystalline SiO₂ (charge of ions 4+ and 2–) was successfully built.⁹ The structure and energy of the oxide within this model were in good agreement with the experimental data.

Recently, the ionic model of non-crystalline oxides has found broad applications. Simulation of the properties of many simple and complex oxides as well as of related systems (in particular, oxyfluorides) has been performed. The aim of the present review is to discuss and analyse the results obtained in these studies.

II. Construction of models of oxide systems

1. Interparticle potentials in oxides

The applicability of the ionic theory for the construction of models of oxide systems is determined by a significant difference in the electronegativities of oxygen (3.5 according to Pauling) and the majority of metals (0.9 for Na, 1.0 for Ca, 1.5 for Al, *etc.*). For example, in CaO the difference in the electronegativities is ~2.5 and the ionicity of Ca–O bond is close to 76%. For SiO₂, the ionicity is ~51%. Somewhat simplifying the situation, one may therefore assign a formal charge of $-2e$ (where e is the electronic charge) to oxygen atoms, and $+2e$, $+3e$, $+4e$ to Ca, Al, and Si, respectively. In the case of an ionic bond, the interparticle potential is paired, and it is usually written in the form of the Born–Meyer potential or the Pauling potential (see, for example, Ref. 10). The Born–Meyer potential is written as:

$$u_{ij}(r) = Z_i Z_j \frac{e^2}{r} + B_{ij} \exp\left(-\frac{r}{R_{ij}}\right) - \frac{C_{ij}}{r^6} - \frac{D_{ij}}{r^8}, \quad (1)$$

where r is a distance between the centres of ions i and j , Z_i , Z_j are the charges of i th and j th ions, respectively (expressed in elementary charge units e), B_{ij} and R_{ij} are parameters accounting for the repulsion of the ionic shells, C_{ij} and D_{ij} are parameters accounting for the dipole-dipole and dipole-quadrupole interactions, respectively. A special form of the potential (1) is the Born–Meyer–Higgins potential (BMH)¹⁰ in which B_{ij} and R_{ij} are expressed through the ion radii r_i and r_j :

$$B_{ij} = b \left(1 + \frac{Z_i}{n_i} + \frac{Z_j}{n_j}\right) \exp\left(\frac{r_i + r_j}{R_{ij}}\right), \quad (2)$$

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where $b = 0.211$ eV, n_i and n_j are numbers of electrons in the outer filled electron shells of the i th and j th ions, respectively (2 for Li, 8 for O, *etc.*). One of the important properties of the potential (1) is that it decreases at small distances for oppositely charged ion pairs. When $r \rightarrow 0$, the second term in the expression (2) approaches B_{ij} and the first term approaches $-\infty$. These potentials should be applied with care to prevent a probable collapse of the system (unlimited approach of ions) in the simulations. It was shown¹¹ that the collapse can occur when B_{ij} is less than a certain critical value ($B_{ij} < B_{ij}^{\text{cr}}$). This critical value for a M_mO_n oxide is defined by formula

$$B_{ij}^{\text{cr}} = -\frac{Z_i Z_j e^2}{0.5413 R_{ij}}. \quad (3)$$

Usually it is assumed that $R_{ij} = 29$ pm.⁹

However, the collapse may occur even for $B_{ij} > B_{ij}^{\text{cr}}$ in the simulations of strongly compressed systems, if the distance between oppositely charged ions becomes less than r_* , which is the position of the maximum of the potential (1) defined as

$$r_*^2 \exp\left(-\frac{r_*}{R_{ij}}\right) = -Z_i Z_j e^2 \frac{R_{ij}}{B_{ij}}. \quad (4)$$

The Pauling potential is written as:

$$u_{ij}(r) = \frac{Z_i Z_j e^2}{r} + \frac{B_{ij}}{r^n} - \frac{C_{ij}}{r^6} - \frac{D_{ij}}{r^8}. \quad (5)$$

Here n is a parameter ranging, as a rule, from 8 to 10. The Pauling potential approaches infinity when $r \rightarrow 0$, and hence collapse is impossible.

The values of the BMH and Pauling potentials for systems close to oxides (alkali metal halides) were first determined by Fumi and Tosi.^{10,12} The refinement of these parameters was performed according to the known experimental characteristics of the crystalline compounds, such as density, compressibility, and the energy of the system. The precision of the simulations with the BMH potential appeared to be higher than with the Pauling potential. Generally the terms that take into account the dipole-dipole and dipole-quadrupole interactions play a minor role in (1). For instance, the total energy for liquid KCl at 1045 K is -730.2 kJ mol⁻¹, and the contributions of the corresponding interactions are -26.5 kJ mol⁻¹ and -4.1 kJ mol⁻¹ (see Ref. 13). In oxide systems, these terms are even less important and therefore they are often neglected.

The parameters of the Born–Meyer potentials for crystalline MO oxides ($M = \text{Mg, Ca, Sr, Ba}$) were calculated from the values of cell parameters and dielectric constants.¹⁴ Pair potentials for these oxides and for SiO_2 , UO_2 , TiO_2 , Nb_2O_5 , and silicates were considered.¹⁵ The parameters of the interactions in $M\text{--O}$ pairs ($M = \text{Mn, Fe, Co, and Ni}$) were also estimated.¹⁶

Despite their simplicity, the potentials (1) or analogous potentials with the additional terms of the Morse type may be used for a description of crystal structures of quartz, cristobalite, boron oxide, as well as the structures of liquid oxides in systems like $\text{Na}_2\text{O--B}_2\text{O}_3$ and $\text{CaAlSi}_2\text{O}_8$ (anorthite).¹⁷

If the simulation does not require calculations of the energy of the system and related characteristics, then the knowledge of the force functions $F(r) = -du/dr$ is sufficient. In a series of studies (see, for example, Ref. 18) Pauling type force functions were applied:

$$F_{ij}(r) = \frac{Z_i Z_j e^2}{r^2} \left[1 + \text{sgn}(Z_i Z_j) \left(\frac{r_i + r_j}{r} \right)^n \right], \quad (6)$$

here the sgn is equal to $+1$ or -1 depending on the sign of the argument ($Z_i Z_j$) and the parameter n varies in the range from 8 to 10.

More complicated pair potentials similar to the Born–Meyer potentials were proposed for silica.¹⁹ Potential parameters were adjusted to give agreement with the experimental data on the stability of α -quartz, α -cristobalite, coesite, and stishovite crystals.

The interaction potentials for $M\text{--O}$ pairs ($M = \text{Ca, B, Al, Si, V}$) were calculated²⁰ using the ‘magic’ Mulliken formula,²¹ which takes into account the mixed ion-covalent character of bonding. The calculated dependences of the potentials on r were approximated by the Pauling expression:

$$U_{ij}(r) = \frac{Z_i Z_j e^2}{r} \left[1 + \text{sgn}(Z_i Z_j) \left(\frac{r_i + r_j}{r} \right)^n (n+1)^{-1} \right]. \quad (7)$$

For all oxides n was taken to be equal to 10. The calculated formal charges did not agree with the normal oxidation states of the metals:

Oxide	Z_1	Z_2	r_1/pm	r_2/pm
CaO	1.46	−1.46	102.0	133.0
B ₂ O ₃	2.34	−1.56	10.0	140.0
Al ₂ O ₃	2.55	−1.70	42.5	140.0
SiO ₂	2.30	−1.15	30.1	120.4
V ₂ O ₅	3.65	−1.46	40.1	133.0

where 1 refers to M and 2 refers to O.

The optimisation of Z_i and r_i according to results of quantum-chemical calculations of ternary systems including Ca, B, Al, Si, V, and O was also performed.²⁰ In particular, the values of $Z_{\text{O}} = -1.46$, $Z_{\text{Si}} = 2.92$, and $Z_{\text{V}} = 3.65$ were obtained. Further, the MNDO quantum-chemical method was applied for calculation of ion-covalent pairwise and three-particle interaction profiles in oxides of silicon, aluminium, phosphorus, *etc.*^{22–26} In a number of other studies, the selection of effective ion charges smaller than the standard oxidation state also allowed one to obtain reasonable agreement between the calculated and experimental structural data for non-crystalline oxides in the framework of the pair interaction model, which indirectly takes into account the mixed ion-covalent character of bonding. However, the use of this model of the interpretation of ‘intermediate’ bonding may prevent calculations of the thermodynamic properties.

The Born–Meyer potentials were used in a simulation of the structure and properties of LiNbO_3 and KNbO_3 (see Ref. 27). For all ion pairs it was taken that $B_{ij} = 1822$ eV and $R_{ij} = (r_i + r_j)/12.36$. Ionic charges and radii were adjusted to give the best agreement with the experimental phonon spectra. For oxygen atoms in KNbO_3 , it was necessary to take two r_i values in two different sites in the unit cell. The formal charges Z_{O} strongly deviate from the common value of -2 . For $\text{Li}_2\text{O--B}_2\text{O}_3$ system, the BMH-type pair potentials were used. Ionic radii were chosen equal to 93 (Li^+), 74 (B^{3+}), and 142 pm (O^{2-}); the charges were equal to 1, 3, and -2 , respectively.²⁸

Interparticle interactions in the covalent bonding model are usually described on the basis of three-particle potentials. The energy of the system is written as

$$U = U_0 + C_2 \sum_i \sum_j u(r_i, r_j) + C_3 \sum_i \sum_j \sum_k v(r_i, r_j, r_k), \quad (8)$$

where U_0 is the energy of the ideal crystal,[†] C_2 and C_3 are coefficients, $u(r_i, r_j)$ and $v(r_i, r_j, r_k)$ are bond stretch and angle distortion terms, respectively. The C_2 and C_3 coefficients were chosen to give the best agreement of the simulated and the experimental characteristics of the oxide (vibrational spectra and internuclear distances). The simplest form for $u(r_i, r_j)$ and $v(r_i, r_j, r_k)$ functions was suggested by Keating,²⁹ *viz.*,

$$u(r_1, r_2) = |\mathbf{r}_1 - \mathbf{r}_2|^2 - d_0^2,$$

where $\mathbf{r}_1$ and $\mathbf{r}_2$ are the radii-vectors of neighbouring ions, and d_0 is the equilibrium bond length, and

[†] The ideal crystal means the crystal with the equilibrium values for all bond lengths and angles; the equilibrium bond angle depends on the type of the crystal lattice.

$$v(r_i, r_j, r_k) = [\cos\theta(ijk) - \cos\theta_0(ijk)]^2, \quad (9)$$

where $\theta(ijk)$ is the angle between $i-j$ and $j-k$ bonds, and $\theta_0(ijk)$ is the corresponding equilibrium angle. The summation in (8) is over the nearest neighbours of the central particle. The three-particle potential is especially often used for silicon (see, for example, Ref. 30). In ionic bonding model, the choice of the initial state for a model is of little importance (it could be either a crystal lattice or a random ionic system), but in the 'covalent version', special initial state should be chosen with fixed coordination numbers (for instance, 4 for Si and 2 for O). This selection of the initial state is usually required in simulation of loose systems by the Reverse Monte Carlo method.

For silica³¹ the pairwise Mie potential was used.³²

$$u = ar^{-n} - br^{-m},$$

where $10 \leq n \leq 12$ and $4 \leq m \leq 6$; and for a three-particle contribution, the Axilrod–Teller potential was applied, which describes the interaction of three dipoles:³³

$$v = c(3\cos\alpha\cos\beta\cos\gamma + 1)(r_1r_2r_3)^{-3},$$

where r_1, r_2, r_3 are the sides of a triangle formed by dipoles, α, β, γ are its angles, and c is a fitting parameter. The coefficients for low- and high-temperature modifications of cristobalite and quartz were adjusted according to the experimental data for SiO_2 . For the Si–Si pairs, the data for pure Si were used and the $u(r)$ potential was chosen in the Lennard–Jones form. A model of pure silicon, which is stable in the diamond lattice, was obtained as a result. For the O–O pairs, the properties of O_2 and O_3 molecules (Lennard–Jones potential) were used. Within this scheme, the dissociation energy of oxygen molecule obtained was in agreement with the experimental data, but the stable configuration for O_3 appeared to be linear rather than triangular. For the Si–O pairs, the Lennard–Jones potential was also used. Other parameters of the model were refined to achieve agreement between the calculated and the experimental results for the properties of the crystalline silica. *Ab initio* potentials were used³⁴ to describe the lattice parameters and melting points of the MgO , Mg_2SiO_4 , and MgSiO_3 oxides.

In a number of studies, combined potentials were used that take into account both ionic and covalent contributions in oxides. A combination of the Keating potential (9) for the triatomic combination that included Si and O, and the Lennard–Jones potential for Na–Si and Na–O pairs were used to simulate Na_2O – SiO_2 glasses.³⁵ A similar approach was utilised to simulate glasses of the Na_2O – B_2O_3 type (see Ref. 36). For O–B–O and O–B–B triatomic combinations, the three-particle potential was selected, and for pairs including Na atoms the pairwise Born–Meyer potential (1) was chosen.

Data discussed above show that the choice of the interparticle potential is arbitrary to some extent. After this choice, the values of parameters of the potential can be determined quite accurately from the properties of a crystal or liquid. The more complicated the form of the potential, the more difficult the determination procedure of its parameters and the more specific the potential itself.

2. Specific features of model construction for oxides

If a bulk phase rather than a small cluster is under consideration, the models are placed in the basic cube with periodic boundary conditions, the calculations of the Coulomb terms of the energy and interaction forces is to be done by summing according to Ewald, taking into account all particle pairs in the cube (see, for example, Refs 6, 13, 37, and 38). The procedure of Ewald summation gives high accuracy, but it is time consuming. Thus, some approximations were proposed which described not only spherically symmetrical terms, but also cubic symmetry corrections. For example, the Hansen approximation³⁹ represents the interaction energy in the form of exponential-polynomial series giving an error of about 0.1%. Attempts to restrict the Ewald sums by spherically symmetrical part of the potential generally

lead to substantial losses in accuracy,^{40,41} though to more rapid calculations.

For construction of models at temperatures $T > 0$, MD and MC methods are used. Models of amorphous phases at $T = 0$ K can be adequately built with the algorithm of Continuous Static Relaxation (CSR).⁴² In this algorithm, the particles are shifted along the overall force by a certain value on each step. The magnitude of the shift is chosen so as to provide an efficient system relaxation. Initial shift may be large (for instance, 50 pm), but as the equilibrium state is approached it gradually decreases to ~ 0.1 – 1 pm. The shift should be decreased in the case when the monotonic decrease in the potential energy of the system ceases. The CSR method has the same disadvantages as MD: it does not guarantee that the global energy minimum is reached, however at low temperatures it allows one to reach substantially more stable states than the MD method.⁴²

III. Main structural characteristics of non-crystalline systems

The main structural characteristics of non-crystalline multicomponent systems are partial pair correlation functions (PPCF) $g_{ij}(r)$, which give the probability of occurrence of a pair of i and j particles at a distance r . They are normalised to give $g_{ij}(r) \rightarrow 1$ when $r \rightarrow \infty$. These functions are directly calculated in MD and CSR methods. The distribution of azimuthal $\theta(\text{BAC})$ angles for B–A–C three-atomic systems in which B and C atoms are the closest neighbours of the central A atom can be also calculated. These distributions are especially informative for loose systems with chain or network structures. Construction of Voronoi polyhedra^{43,44} for loose systems is of little interest due to their high diversity; none of the polyhedra type is more abundant in these systems.

Analysis of polymerisation processes is performed by building up bound groups, which allows one to reveal complex ions such as SiO_4^{4-} , $\text{Si}_2\text{O}_7^{6-}$, etc., which are formed in silicates as time-stable moieties. In the search for the bound groups, the Si–O distance (r_c) should be defined. This distance determines the closest neighbours of the central particle and usually coincides with the first minimum position of the corresponding PPCF. The cyclic part of the structure can be found and the distribution of rings along the overall structure can be calculated in a similar way. The cycle included only neighbouring particles at distances not longer than r_c .

Topological looseness of a system can be characterised by two parameters, viz., ρ_1 and s .⁴⁵ The parameter ρ_1 is defined as the mean height of the first peaks in the PPCF.

$$\rho_1 = \frac{\sum X_i X_j r_1(ij)}{d_0}, \quad (10)$$

where X_i and X_j are the ionic parts for the i th and j th particles, respectively, $r_1(ij)$ is the position of the first maximum in the PPCF of the ij pairs, summation is done over all pairs of particles, and $d_0 = (V/N)^{1/3}$, N is a number of particles in the volume V . Topologically dense systems (simple liquids, liquid and amorphous metals, non-crystalline alkali metal halides, etc.) have $\rho_1 = 1.08 \pm 0.02$ and loose systems have $\rho_1 < 1.05$. For the loosest systems, such as amorphous carbon, the ρ_1 value is 0.608.⁴⁶

The second parameter is defined by ratio $s = g_1/g_{1d}$, where g_1 is a mean value of the first maxima heights of the PPCF and g_{1d} is the corresponding value for a dense system calculated according to the widths of the first maxima of the PPCF.⁴⁵ Topologically dense systems have $s \approx 1$, while for loose systems $s > 1$.

There are a number of other physicochemical characteristics of the systems considered, which are often studied by computer simulations. They include self-diffusion coefficients of particles, viscosity, autocorrelation functions of velocities, flows, etc., which allow calculations of vibrational spectra and their comparison with the experimental data on elastic and inelastic scattering of

radiation. Studies of this kind for oxide systems are relatively rare (see, for example, Refs 1–6).

The role of Coulomb interactions in the structure formation and its influence on some properties of non-crystalline ionic systems were investigated.^{47,48} LiCl–KCl eutectics were analysed⁴⁷ with Coulomb interactions ‘switched on’ and ‘switched off’ (the BMH potentials were used). It was demonstrated that for a neutral system the positions of the first maxima of the PPCF for all pairs depend on the particle size and increase on going from Li to K. Taking account of the Coulomb interactions (for the same volume) results in a drop of pressure and a decrease in self-diffusion coefficients by a factor of 2–5 and an increase in lifetime of the first coordination spheres of Li and K by a factor of 1.5–3.

Gradual changes in the structure and the thermodynamic properties of a liquid on going from the ideal gas state to the ionic model state of an MO oxide were considered.⁴⁸ The density of a system corresponded to that of liquid MgO. Particle interactions were described by Eqn (1) with the variables $B_{ij} = B$ and $Z_1 = -Z_2 = Z$. The influence of these parameters on the shape of PPCF, coordination numbers (CN), topological characteristics, and thermodynamic properties was considered. It was established that the growth of B leads to a monotonic increase in the PPCF peak heights. If $B < 600$ eV and $Z = 0$, the structure of the liquid appeared to be loose ($\rho_1 < 1.01$). On going from the ideal gas state to an MO system with neutral particles at constant volume and temperature, the entropy decreased by $3.43Nk$ (where N is the number of particles in the model, k is the Boltzmann constant). On further transition to the ionic system with $Z = 2$, it decreases additionally by $1.76Nk$. Therefore, the Coulomb interactions give a somewhat smaller contribution to the entropy of a liquid than the repulsion of ionic shells.

IV. Models of simple non-crystalline oxides

M₂O and MO oxides do not form glasses on ordinary cooling of liquids. Diffraction studies (hereinafter, X-ray and neutron diffraction methods are meant) of these liquid oxides, to our knowledge, have not been performed. Oxides of M₂O₃ (B₂O₃, Al₂O₃), MO₂ (SiO₂, GeO₂), M₂O₅ (P₂O₅, Nb₂O₅, Ta₂O₅), and MO₃ (WO₃) types have been intensely studied by the methods mentioned. The number of studies of silica and boron oxide is especially large.

1. Models of silica

According to diffraction data,^{49–51} liquid and amorphous SiO₂ have the structure of a tetrahedral network with the coordination number for Si–O pairs $z(\text{Si–O}) = 4$. The structural element of the network is a nearly tetrahedral complex SiO_4^{4-} , the adjacent tetrahedra are attached to each other through the shared vertices so that oxygen atoms have coordination numbers $z(\text{O–Si}) = 2$. The most serious defects in this structure are silicon atoms with coordination number $z(\text{Si–O}) = 3$.⁵²

The first ionic model of SiO₂ that used the Born–Meyer pair potentials was constructed in 1976.⁹ The charges of Si and O were equal to 4 and –2, respectively. The model contained 162 ions in the basic cube with periodic boundary conditions. The MD method with Ewald’s account for the Coulomb interaction was applied. The B_{ij} parameters of the potential (1) for Si–Si, Si–O, and O–O pairs were equal to 2055.4, 1729.5, and 906.5 eV, respectively. First, heating of the system up to 6000 K was simulated in order to accelerate the diffusion of particles. After relaxation, cooling of the system to 300 K was simulated. In this way, a model of glass-like silica was obtained. The PPCF for a model of SiO₂ obtained with similar potentials⁵³ are shown in Fig. 1. The position of the first peak for Si–O pairs is ~ 162 pm, which is in accordance with the experimental data.^{49–51} It is noteworthy, that the energy[‡] of the model ($-12\,240$ kJ mol^{–1}

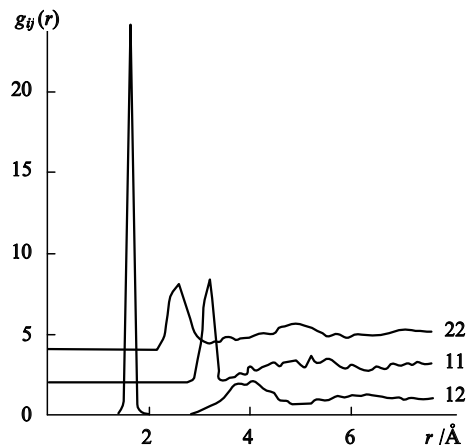


Figure 1. Partial pair correlation functions for the models of amorphous silica at 0 K (CSR method).

The curves are shifted along the ordinate axis; numbers denote pairs of ions (1 states for Si, 2 for O).

relative to ions at infinite distance) is very close to the real value ($-13\,300$ kJ mol^{–1}). This means that the ionic model describes the real situation adequately.

Ion models containing 375 and 3000 ions in the basic cube were constructed.^{54,55} Simple force functions in the form (6) were applied. Values of $Z_1 = +2.272$ and $Z_2 = -1.136$ had to be chosen to achieve agreement with the diffraction data. First, relaxation of liquid SiO₂ at 3000–7000 K was simulated by the MD method. Subsequent cooling to ~ 1500 K resulted in a glass-like state with the structure of a tetrahedral network. Model PPCF were in good agreement with the X-ray data on the peak positions. It was demonstrated that at 300 K the distribution of O–Si–O azimuthal angles has a maximum at $109.5 \pm 10^\circ$ and that of Si–O–Si at $151 \pm 18^\circ$. The structure of SiO₂ is loose and contains cavities (pores) with a mean radius of 93 pm. Jumps in heat capacity, pressure, and self-diffusion coefficient observed for the model at ~ 1500 K were attributed to a glass transition.

An autocorrelation function of velocities and, from this function, density of vibrational states, were calculated for amorphous silica.⁵⁵ However, no agreement with the experimental data on neutron scattering was achieved. It was found⁵⁶ that the Keating potential (9) matches best to a reconstruction of the vibrational spectrum. Good agreement with the experimental data was also obtained for a model with 750 particles.⁵⁷ The calculated vibrational spectra for Si⁴⁺ and O^{2–} ions⁵⁸ differ somewhat from the measured ones.

The statistics of pore distribution and the character of their aggregation into the bigger cavities (‘trees’) in amorphous silica were investigated on a model composed of 648 atoms.^{59,60} Pore radii appeared to be in the range of 18–183 pm. A series of overlapping pores was considered to be a tree. It was demonstrated that the number of ‘trees’ decreases rapidly with the increase in a pore number (N) in a ‘tree’ ($N = 3–20$). The longest trees have approximately linear shape.

The presence of pores in the structure of silica plays an essential role. Ionic admixtures occupying these pores may enlarge their sizes and affect density fluctuation of the silicon-oxygen network. The appearance of a first sharp diffraction peak in structural factor of silica at magnitude of the scattering vector of $K \approx 15$ nm^{–1} was explained by the presence of pores.⁶¹ This assumption was examined⁶² by the MD simulation of (MO)_x(–SiO₂)_{1–x} (M = Li, Na) solutions with $x = 0.18–0.67$. Each model contained 216 Si particles. Admixture atoms occupied the pores of the silicon-oxygen network. The intensity of the first sharp diffraction peak increased linearly as the Li atoms concentration increased and decreased on addition of sodium. This

‡ Hereinafter the following notations will be used in the discussion: E , E_{coul} , E_{kin} , E_{sh} , which stand for the total, Coulomb, and kinetic (thermal) energies and energy of repulsion of electron shells, respectively.

behaviour is due to the ratio of neutron scattering lengths on pores and impurity atoms.

A model of amorphous SiO₂ (246 ions) was also constructed by the CSR method.⁶³ Later, models of liquid and amorphous silica containing 498 ions each in the basic cube were constructed.^{53, 64–66} The pair potentials (1) were used (without the two last terms) with the values of $B_{11} = 0$, $B_{12} = 1729.5$, $B_{22} = 1500$ eV, and $R_{ij} = 29$ pm. Coulomb interactions were taken into account by the Ewald–Hansen method. First, a heating of the system up to 6000–9000 K was simulated to reach the equilibrium structure and then the temperature was lowered to 2000 K. The length of MD-sweeps was 500–1000 time steps (one time step is 2.04 fs). The values of the total energy for models of SiO₂ with different numbers of particles (n) at $T = 0$ K obtained in different studies (scaled for equal B_{ij} coefficients) are compared below.

$-E/\text{kJ mol}^{-1}$	n	Ref.
12245	162	9
12487	246	63
12414	498	53

For the two last models, the energy differs by only 0.58%, which exceeds insignificantly the computational error. In another study,⁹ the energy is higher by ~ 200 kJ mol⁻¹, i.e. this model is less stable. The differences may be caused not only by the different number of particles, but also by a different degree of approach of the system to the equilibrium.

Table 1 shows the characteristics of silica calculated at 0 K and 2000 K and those found experimentally at 300 K. It is clearly seen that the ionic model of SiO₂ with the potentials (1) and (2) allows one to obtain altogether reasonably good agreement with the experimental results. Coordination numbers of Si⁴⁺ ions are distributed as follows:

$z(\text{Si}-\text{O})$	3	4	5
Number of Si ⁴⁺ ions	7	152	7

Thus, $\sim 8.4\%$ of silicon atoms have a coordination number (CN) equal to 3 or 5, but the majority of Si atoms are surrounded by four oxygen atoms. In the real non-crystalline silica the number of 'defective' silicon ions is much less. Coordination numbers of 4 and 2 were determined by Della Valle and Andersen.⁶⁷ The mean value of O–Si–O angle in the models is close to the tetrahedral (109.5°). Therefore, the structure of silica is a tetrahedral network. According to the values of the topological parameters ρ_1 and s , this structure is rather loose. If a volume of silica is contracted by a factor of ~ 2.5 , then the ρ_1 value becomes equal to 1.08 and the structure turns dense, similar to the structure of metal glasses.¹¹

Models of liquid silica at temperatures of 2100 K and 6000 K and densities 2.2–4.0 g cm⁻³ were constructed.⁶⁸ Coulomb interactions were taken into account by the Ewald summation. The p – V isotherms, structural characteristics, self-diffusion coefficients of ions, density of vibrational states, and IR absorption spectra were calculated. A study of SiO₂ structure at 6000 K and pressures up to 35 GPa by the MD method indicated⁶⁹ an increase in ordering of the melt structure and in the coordination

numbers with the increase in pressure. It was demonstrated that compression of the glass noticeably changes the ring statistics.⁷⁰

The existence of a close correlation between ρ_1 and s parameters and the trend of the system to glass formation was proposed.^{11, 53} Indeed, the looser the system, the more difficult the crystallisation process (even merely for geometrical reasons). The factors governing the glass transition are evidently kinetic ones. There is also a thermodynamic aspect associated with the driving force of the crystallisation (difference in the Gibbs energies of non-crystalline and crystalline phases). However, for a number of loose structures with $\rho_1 < 1.0$ there is a regularity, which states that a decrease in ρ_1 results in easier glass formation. In particular, low value of ρ_1 (~ 0.9) is the reason for easy glass formation by silica on ordinary cooling in air.

In order to investigate the size effects, big models of amorphous silica with numbers of ions 648, 5184, and 41 472 and density of 2.2 g cm⁻³ were constructed using the MD method.⁷¹ Pair potentials of the Pauling type, but with shielded Coulomb interactions and including ion polarisability, were used. In addition, the three-particle interactions were introduced by the method of Stillinger and Weber.⁷² As a result, 19 potential parameters had to be adjusted. Heating of β -cristobalite up to 12 000 K and its gradual cooling to 300 K were simulated. The calculated structural factor (SF) of the model was in very good agreement with the data on neutron scattering. The agreement for PCF was also good. It was demonstrated that the size of the system does not affect the PPCF shape of the model, although structural factors differ slightly in the region of the scattering vectors of 15–55 nm⁻¹. The height of the first distinct peak of SF at the scattering vector $K = 15$ nm⁻¹ increases slightly with increase in the size of the system (from 1.25 to 1.48) and for $N = 41$ 472 it is in excellent agreement with the experimental value. The density of vibrational states in SiO₂ was calculated⁷¹ by diagonalisation of the dynamic matrix.⁷³

Destruction of amorphous and crystalline silica have been simulated.⁷⁴ Models of porous silica with different densities were also investigated.⁷⁵

2. Models of boron oxide

According to diffraction analysis data,^{49, 51, 76, 77} amorphous B₂O₃ has a layered structure with average CN of B–O pairs equal to 3. The first peak of the total PCF (TPCF) for X-ray radiation, which corresponds to B–O pairs, is located at 137–138 pm. The second peak corresponds to O–O pairs (237 pm). An isosceles triangle with sides of 138, 138, and 237 pm contains the obtuse angle of *ca.* 120°. Therefore, BO₃ groups have to be almost planar triangles. These triangles are fused by shared vertices (oxygen atoms). In the glass-like boron oxide, the presence of boroxol B₃O₃ rings with angles inside the ring of $\sim 120^\circ$ was proposed.⁵⁰ Addition of Na₂O to B₂O₃ leads to an increase in coordination number of boron from 3 to 4 and to a decomposition of the initial structure.⁴⁹

The structure of the B₂O₃ glass was also investigated by NMR method using ¹¹B isotope (see Ref. 78). Boron sites of two types with ratio 2:1 were observed. The first type was assigned to boroxol rings and the second one to BO₃ groups; and these structural elements are present in equal ratios. O–B–O angles for these two configurations are similar. However, the chemical shifts for the sites of two types are different due to the longer B–O bonds in the rings as compared to BO₃ groups.

Basing on NMR data and model calculations of the correlation functions, it was shown^{79, 80} that the B₂O₃ glass can contain more extended elements of local ordering than the BO₃ groups and boroxol rings, in particular, B₃O₇, B₃O₈, B₄O₉, B₅O₁₀, B₅O₁₁, and B₅O₁₂ in which the boron atoms may have CN of 3 and 4. In this case, simulations give a glass density close to the experimental value which could not be achieved using purely boroxol model.

It should be taken into account that nanometer-scaled structural inhomogeneities revealed in real glasses or melts by, for example, small angle scattering cannot be reproduced on relatively small models with the basic cube edge of ~ 2 nm. Using this

Table 1. Calculated and experimental parameters for ionic models of silica.

Parameter	Calculation ⁵³		Experiment ^{49, 50} 300 K
	0 K	2000 K	
$r_1(\text{Si}-\text{Si})/\text{pm}$	319	317	312
$r_1(\text{Si}-\text{O})/\text{pm}$	161	162	162
$r_1(\text{O}-\text{O})/\text{pm}$	257	259	265
$\theta(\text{O}-\text{Si}-\text{O})/\text{deg}$	109.2 $\pm$ 12.9	109.1 $\pm$ 14.6	109.5
$\theta(\text{Si}-\text{O}-\text{Si})/\text{deg}$	154.8 $\pm$ 14.7	152.7 $\pm$ 14.5	147.0 $\pm$ 16.0
ρ_1	0.892	0.882	—
s	1.59	1.39	—

method, structures of B_2O_3 (200–270 °C) and of a series of alkali borates and silicates systems were studied.^{81,82} In the case of B_2O_3 , domains with an average size of ~ 1.5 nm and with densities lower than in the surrounding matrix, were found. In alkali borate glasses the inhomogeneities are due to several reasons, viz., thermal density fluctuations, structural inhomogeneities, supercritical concentration fluctuations, and peculiarities of the fusion of high-alkali structural complexes.

Models of amorphous boron oxide were constructed.^{18,83–86} Force functions (6) were introduced for the boron oxide description.^{18,83,84} The parameters were adjusted to obtain the structure with planar triangular BO_3 fragments. The models composed of 320 ions were relaxed during 1000 steps at 6000 K. The diffusion processes in the system occurred very slowly. This could be accelerated by decreasing the ion charges. Two experiments with the models composed of 192 and 1920 ions were carried out. For both models, the temperature was gradually decreased from 2000 to 300 K at constant volume. The energy and pressure decreased during the cooling, and the temperature dependencies of both characteristics could be represented in the form of two linear regions. If the intersection point is identified as the glass transition point and its actual value (~ 540 K) is taken into account, the estimates for the effective charges are $Z_1 = +1.125$ and $Z_2 = -0.75$.

Analysis of the models demonstrated that the values of the azimuthal O–B–O angle lie in the range $119 \pm 6^\circ$ and of the B–O–B angle, in the range $154 \pm 20^\circ$. The rings composed of six and more B atoms predominated in the structure and the boroxol rings B_3O_3 were absent. Almost ideal, centred BO_3 triangles linked through the vertices form an infinite system of layered elements and twisted ribbons.

An attempt to decrease the width of the B–O–B angle distribution in the model of B_2O_3 using a special algorithm was undertaken.⁸⁷ To this end, the values of B–O and B–B bond lengths were fixed at 138 and 239 pm ($239 = 138\sqrt{3}$), respectively. The model comprised 1680 ions. A decrease in temperature from 6000 to 300 K was performed in 5000 steps, 1 fs each. At 300 K, the energy was equal to -2950 kJ (g-at.)⁻¹ instead of -2975 kJ (g-at.)⁻¹ without fixing the bond lengths. The heat capacity of the model with the fixed bond lengths was equal to 10.3 J (g-ion K)⁻¹ instead of 24.5 J (g-ion K)⁻¹ with the usual algorithm. The final structure of the glass did not contain the six-membered boroxol rings. Therefore, the mere fixation of B–O–B angles (120°) does not lead to the formation of these rings. The structure of boron oxide is a result of a fusion of BO_3 triangles by shared vertices. The planes of neighbouring triangles are non-coplanar, and the most probable angle between them is 90° . It was shown⁸⁵ that a decrease in the rate of cooling in the simulation by six orders of magnitude leads to an increase in the glass density, but it hardly affects the ordering of the structure.

Models of liquid and amorphous B_2O_3 were also constructed.^{64,88} The models comprised 500 ions in the basic cube. The potentials (1) with the account for the Coulomb interactions according to Ewald–Hansen³⁹ were applied. The potential parameters were as follows: $Z_1 = +3$, $Z_2 = -2$, $B_{11} = 0$, $B_{12} = 800$ eV, $B_{22} = 1500$ eV, and $R_{ij} = 29$ pm. Characteristics of B_2O_3 calculated for 0 K and 2000 K and the experimental values are shown in Table 2.

Partial pair correlation functions for the model of liquid B_2O_3 at 1473 K are depicted in Fig. 2. Simulated $r_1(ij)$ distances are in very good agreement with the experimental data. Coordination numbers were the same as in Ref. 18: $z(B-O) = 3$ and $z(O-B) = 2$ (with the closest neighbour sphere radius of 200 pm). The distributions of the O–B–O and B–O–B azimuthal angles are Gaussian ($116 \pm 10.3^\circ$ and $154.2 \pm 12.2^\circ$) and are similar to those found earlier.¹⁸ Structural characteristics of the liquid oxide at 2000 K differ only slightly from those calculated at 0 K (see Ref. 64). Topological characteristics of the models indicate the looseness of the structures of both liquid and amorphous boron oxide. It is less dense than the structure of silica. The basic

Table 2. Calculated and experimental parameters of B_2O_3 .

Parameter	Calculation ^{64,88}		Experiment ⁴⁹
	0 K	2000 K	
$V/\text{cm}^3 \text{mol}^{-1}$	38.43	45.80	38.6
P/GPa	~ 0	~ 0	~ 0
$E_{\text{coul}}/\text{kJ mol}^{-1}$	-21718	-21665	—
$E_{\text{tot}}/\text{kJ mol}^{-1}$	4417	4332	—
$r_1(ij)$ for pairs			
B–B	267	267	(270)
B–O	139	138	138
O–O	235	239	237
ρ_1	0.830	0.787	—
s	2.21	3.16	—

structural elements are almost planar BO_3 groups fused through shared vertices. In the model of liquid B_2O_3 four four-membered, five six-membered, and seven eight-membered rings were found.

The molar volume for the model of amorphous B_2O_3 is close to its actual value. However, the calculated atomisation energy for the model is 1383.1 kJ mol⁻¹, while the experimental value⁸⁹ for B_2O_3 crystals is 2737.1 kJ mol⁻¹. The difference between these values is 7.8% of the total energy and can not be attributed to the amorphisation energy of crystal. Probably, it indicates the greater contribution of covalent bonding in boron oxide. The value of energy at 300 K ($-14\,875$ kJ mol⁻¹)⁸⁷ is substantially higher than that found in other studies.^{64,88}

New interparticle potentials for boron oxide were proposed;⁹⁰ their parameters were adjusted using the method of linear programming. For better description of the properties of various crystal phases, terms depending on CN were included. This method allowed one to predict new stable polymorphous forms of crystalline B_2O_3 with a high content of the boroxol rings (up to 100%). These potentials were applied for the construction of a B_2O_3 glass model with an increased concentration of these rings.⁹¹ Seven different potentials (including three-particle ones) were used⁹² for construction of an MD model of B_2O_3 (424 particles). Structures of the models proposed appeared to be similar to each other and were close to the real one. Nevertheless, the dynamic properties of the system (vibrational modes) were reproduced correctly only in the case when the three-particle contributions were taken into account.

A process of glass formation in boron oxide and some borates on cooling from a liquid state was investigated using MD method.⁹³ The properties of the phase were described with Prigogine–Defay parameter (γ), which establishes the correlation between the glass transition point and the ordering parameters.⁹⁴ For the system studied $\gamma > 1$. It was shown, that the formation of B_2O_6 groups results in a decrease of γ , and the formation of groups

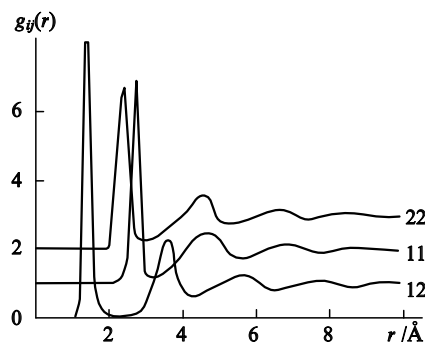


Figure 2. Partial pair correlation functions for the model of liquid B_2O_3 at 1473 K.

The curves are shifted along the ordinate axis; numbers denote pairs of ions (1 states for B, 2 for O).

with terminal oxygen ions (which have only one neighbouring boron atom) results in an increase of γ .

3. Models of non-crystalline Al_2O_3

The structure of liquid Al_2O_3 has not been studied experimentally due to its high melting point. In the bulk, alumina does not form glass. Amorphous oxide is formed only as thin films (for example, in anodic oxidation of the aluminium). Data by different authors on the structure of Al_2O_3 are only in partial agreement. An electronographic study of films obtained by anodic oxidation in boric acid-containing electrolyte was reported.⁹⁵ Peak positions in the total PCF (TPCF) were equal to 175, 275, and 320 pm. The first peak corresponds to Al–O pairs, the second one to O–O, and the third one to Al–Al pairs. Similar films with a thickness of 5 nm were studied⁹⁶ at the maximum scattering vector $K = 185 \text{ nm}^{-1}$. Peak positions in the TPCF were 182, 310, and 420 pm. The mean CN were as follows: $z(\text{Al–O}) = 6$ and $z(\text{O–Al}) = 4$. Therefore, virtually all aluminium atoms were in an octahedral environment.

For a film with thickness of 150 nm (after separation),⁹⁷ the peak positions were at 180 and 320 pm, and $z(\text{Al–O}) = 5.5$. Such an arrangement of particles is typical of γ' - Al_2O_3 crystal modification. An approximate interpretation gave the following results:

Pair	Al–Al	Al–O	O–O	Al–O(2)
$r(ij) / \text{pm}$	315	180	261	345
CN	10.3 ± 0.2	5.4 ± 0.1	12.0 ± 0.1	9.1 ± 0.2

The notation Al–O(2) relates to the second peak of the Al–O pairs. These data are close to the results of another study.⁹⁵

The following groups: AlO_4 , AlO_5 , and AlO_6 were found in a transitional amorphous phase α - Al_2O_3 using NMR ^{27}Al (see Ref. 98).

A model of amorphous Al_2O_3 incorporating the structural data⁹⁶ has been constructed.⁹⁹ The model contained 150 particles in a sphere with a diameter of $\sim 150 \text{ pm}$. First, the particles were arranged in a quasirandom order with limitations on the minimum interparticle distance, CN, azimuthal angles, and the type of neighbours. Further relaxation of the model was performed by the Reverse Monte Carlo method. In the structure obtained, the distribution of the Al–O–Al angles had maxima at 60, 80–100°, and 120–130°, and the maxima of distribution of the O–Al–O angles were at 80–100°, 130–140°, and 150–160°. Taking into account the small size of the model, the authors concluded that its structure was similar to that of α - Al_2O_3 . A model of amorphous oxide composed of 120 particles was constructed analogously¹⁰⁰ revealing a layered structure and the formation of clusters of 5- or 6-membered spatial rings in the layers.

An MD model of liquid oxide at $T = 2560 \text{ K}$ with ion charges $Z_1 = +2.55$ and $Z_2 = -1.70$ was constructed.¹⁰¹ The Al–O and O–O distances appeared equal to 185 and 273 pm, *i.e.* slightly longer than the actual values, with $z(\text{Al–O}) = 5.2$.

In a simulation (500 particles) of liquid (overcooled) oxide at 2000 K and of amorphous oxide at 0 K by MD and CSR methods the potentials (1) were applied.⁸⁸ The following parameters were chosen: $Z_1 = +3$, $Z_2 = -2$, $B_{11} = 0$, $B_{22} = 1500 \text{ eV}$ (the same as for models of silicates⁶⁵). The parameter $B_{12} = 1479.86 \text{ eV}$ was adjusted to make the molar volume of corundum at $P = 0$ equal to the actual value. Coulomb interactions were taken into account according to the Ewald–Hansen method.³⁹ The difference between the calculated energy for the ionic model and the energy of the real crystal was only 3.1%, and therefore an interpretation of corundum as the ionic compound is quite reasonable. In a simulation of the amorphous phase at 0 K, the initial CSR step was 50 pm and then it was gradually diminished to 1–2 pm.⁸⁸ About 250 steps were necessary to complete relaxation. The model built had the following parameters:

$V / \text{cm}^3 \text{ mol}^{-1}$	31.2	r_1 / pm for pairs

P / GPa	1.65	Al–Al	312
$E / \text{kJ mol}^{-1}$	–15289	Al–O	175
		O–O	268

The difference in energies of amorphous Al_2O_3 and crystalline corundum, equal to 274 kJ mol^{-1} , is the heat of crystallisation of amorphous Al_2O_3 . The heat of crystallisation of liquid alumina at 2300 K is 109 kJ mol^{-1} (see Ref. 89). These values are in reasonable agreement taking into account the difference in temperatures. The molar volume of amorphous Al_2O_3 is closer to the molar volume of γ - Al_2O_3 crystal (spinel type, $27.83 \text{ cm}^3 \text{ mol}^{-1}$) rather than of α - Al_2O_3 ($25.57 \text{ cm}^3 \text{ mol}^{-1}$). The real density of amorphous oxide films, to our knowledge, have not been measured. The volume of γ - Al_2O_3 increases by $\sim 12\%$ upon amorphisation.

Structural characteristics of models of amorphous alumina are in good agreement with the experimental data.⁹⁵ However, $g_{ij}(r)$ functions determined in independent studies^{88, 101} differ substantially. This is mainly due to the difference in the pair potentials used. Mean CN for the models⁸⁸ are as follows: $z(\text{Al–O}) = 4.47$ and $z(\text{O–Al}) = 2.98$. These values exceed the normal atom valences by factor ~ 1.5 , and therefore an assumption of the presence of a continuous random bond network in the structure of amorphous alumina may be rejected. The value of $z(\text{Al–O})$ is slightly lower than in the γ - Al_2O_3 crystal lattice ($0.7 \times 6 + 0.3 \times 4 = 5.4$), which is typical of dense non-crystalline structures.

Distributions of CN in the amorphous oxide are rather broad. Their calculation with the radius of the closest neighbour sphere of 240 pm gave the following results:

Number of neighbours	1	2	3	4	5	6	7
Number of Al^{3+} ions	–	–	8	102	78	12	–
Number of O^{2-} ions	–	42	222	36	–	–	–

Most of Al^{3+} ions have four and five O^{2-} neighbours, and most of oxygen atoms have three Al^{3+} neighbours. These data do not confirm the suggestion of the existence of such structural elements as the AlO_3 trigonal pyramid.

A model of liquid (overcooled) Al_2O_3 was constructed⁶⁶ using the MD method with the same parameters as in Ref. 88. Coulombic interaction was taken into account according to the Ewald–Hansen method.³⁹ The model contained 500 ions. The calculated molar volume of the liquid oxide at $P = 0$ ($34.3 \text{ cm}^3 \text{ mol}^{-1}$) was very close to the actual value ($34.3 \text{ cm}^3 \text{ mol}^{-1}$ at 2300 K, see Ref. 102). The Al–Al, Al–O, and O–O distances were found to be equal to 313, 174, and 286 pm, so the heating by 2000 K affected noticeably only the O–O pairs. Mean CN of Al–O pairs was equal to 4.50 and their distribution was still very broad. Both at $T = 0 \text{ K}$ and $T = 2000 \text{ K}$, the system had a relatively small number of aluminium ions with octahedral coordination; the predominant values were $z(\text{Al–O}) = 4$ and 5.

The topological characteristics of the Al_2O_3 structure were calculated (see Refs 66 and 88).

T / K	0	2000
ρ_1	1.051	1.056
s	1.16	1.13

Consequently, the structure of non-crystalline alumina lies on the lower boundary of the area of topologically dense systems. This accounts for difficult glass formation in the ordinary cooling of a liquid; ρ_1 and s values contradict the assumption of a layered structure of the oxide.

4. Models of non-crystalline Fe_2O_3

Fe_2O_3 oxide has not been obtained in an amorphous state, and in the liquid state it is unstable and readily decomposes to FeO and oxygen. However, Fe^{3+} ions are present in complex oxides in various concentrations depending on the oxidation potential of the medium. Models of non-crystalline Fe_2O_3 oxide were constructed using MD and CSR methods at 0 K and 2000 K.^{103–106} The models contained 500 ions in the basic cube. The pair

potentials (1) with parameters $B_{11} = 0$, $B_{22} = 1500$ eV, $R_{ij} = 29$ pm were applied, the value of $B_{12} = 2114.2$ eV was calculated

Table 3. Calculated parameters of the models of non-crystalline Fe_2O_3 .¹⁰³

Parameter	0 K	2000 K
$V/\text{cm}^3 \text{ mol}^{-1}$	39.0	40.2
$E/\text{kJ mol}^{-1}$	−14418	−14168
$r_1(ij)/\text{pm}$ for pairs		
Fe–Fe	331	327
Fe–O	191	190
O–O	298	291
$z(\text{Fe–O})$	4.7	4.7
ρ_1	1.07	1.05
s	1.21	1.18

according to the actual density of the crystal with the corundum lattice. The models were constructed in a way similar to that for Al_2O_3 . Table 3 shows the parameters of the models for Fe_2O_3 at 0 K and 2000 K.

The Fe–O distance of 190 pm can be compared with the diffraction data for $\text{Fe}_2\text{O}_3 \cdot 4(\text{Na}_2\text{O} \cdot 2\text{SiO}_2)$ (see Ref. 107) and $\text{CaO} \cdot \text{Fe}_2\text{O}_3$ (see Ref. 108) glasses where it lies in the range of 196–203 pm. In order to elongate the Fe–O distance to 198 pm, the B_{12} parameter was increased to 2453.0 eV.^{104–106}

These data show that the structures of Fe_2O_3 and Al_2O_3 are close to each other. At 0 K, 64 out of 200 iron ions have four neighbours, 105 ions have five, and 31 ions have six O^{2-} neighbours.^{103–106} A relatively big Fe^{3+} ion cannot arrange a rigid group of oxygen ions around it, as takes place in B_2O_3 , and the network of bonds is not created. Slightly increased value of the s parameter is due to the presence of big pores. According to the value of ρ_1 , the structure of non-crystalline oxide is rather dense.

The hysteresis effects in Fe_2O_3 are small. Construction of a model of amorphous oxide at 0 K using the CSR method, an increase in the temperature up to 2000 K using the MD method and consequent cooling back to 0 K led to a decrease in the energy relative to the initial value by only 0.05%.

5. Models of UO_2

Models of crystalline and liquid UO_2 have been constructed (see Ref. 109). A model of rigid ions with charges +4 and −2 has been used. The parameters of the potential (1) were as follows: $B_{11} = 0$, $B_{12} = 869.98$ eV, $R_{12} = 42.7$ pm, $B_{22} = 11272.6$ eV, and $R_{22} = 13.63$ pm for $r < 120$ pm, while at longer distances the potential $u(r)$ was represented in a polynomial form. All potentials were cut off at 520 pm. In addition, the dipole-dipole interactions were included in a potential for U–O pairs.

A model of UO_2 crystal (96 ions in the basic cube) gave a good fit with the experimental data on elastic constants and the dielectric properties. It was shown that the self-diffusion coefficient of O^{2-} ions in the temperature range of 2500–3300 K, while the system is still solid, is of the order of $10^{-5} \text{ cm}^2 \text{ s}^{-1}$, which is typical of liquids, *i.e.* the oxide under these conditions is a superionic conductor. In the liquid state (at 3200–4200 K), the self-diffusion coefficient of oxygen changes from 7×10^{-5} to $1.4 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$, which is 3–4-fold greater than that for the uranium ions. The structure of the oxide has not been described.¹⁰⁹

6. Models of non-crystalline P_2O_5

Phosphate slags are important in metallurgy. Phosphate glasses attract considerable attention due to their prospective use in optoelectronics. P_2O_5 easily forms glasses. It possesses the high viscosity, and its use as an additive allows preparation of glasses with variable composition. The properties of phosphate glasses have been reviewed.^{110–113} Hysteresis of the properties, *i.e.* their

dependence on the prehistory of a sample, is a typical feature of the phosphate glasses.

Experimental data on the structure of phosphate glasses obtained by diffraction methods are rather numerous. Crystalline P_2O_5 is built up either of isolated P_4O_{10} molecules or of infinite layers of tetrahedral PO_4 groups (see Ref. 112). One of bonds between pentavalent phosphorus and oxygen atoms is double. The distance $r_1(\text{P–O})$ determined for a NaPO_3 glass¹¹⁴ is equal to 155 pm. The structure of this oxide is represented by long chains of PO_4 tetrahedra linked with other chains through sodium ions. X-ray studies of $[\text{M}(\text{PO}_3)_2]_n$ ($\text{M} = \text{Zn, Cu, Mn, Ca, Mg}$)¹¹⁵ gave the value of $r_1(\text{P–O})$ of 155 pm, which was virtually independent of the composition. However, the magnesium derivative behaved abnormally. Its density is higher than that calculated from a general linear correlation on the number of the M element in the Periodic Table (2.45 instead of the interpolated value 2.25 g cm^{-3}), and the interionic M–O distance is reduced (190 pm for Zn, 195 for Cu, 220 for Mn, 250 for Ca, and 190 for Mg). The first SF peak for magnesium phosphate appears at $K = 15.5 \text{ nm}^{-1}$ (instead of 17.0 for the other compounds) and is also abnormally high. It was supposed¹¹⁵ that the anomalies of magnesium phosphates are due to the formation of phosphate rings in this glass.

The structure of glasses with a composition $\text{M}(\text{PO}_3)_2$ ($\text{M} = \text{Zn, Mg, Ca, Sr, Ba}$) were investigated by neutron scattering method.¹¹⁶ O–O, P–O, and M–O pairs give the principal contributions into the TPCF (with shares of ~47%, 28%, and 15%, respectively). Separation of the TPCF into partial contributions is ambiguous. Nevertheless, for all glasses it was found that $z(\text{P–O}) \simeq 4$, $z(\text{Ca–O}) \simeq 4$ as well. The most reliable results are those for the P–O and O–O pairs:

Parameter	Zn	Mg	Ca	Sr	Ba
$r_1(\text{P–O})/\text{pm}$	154	153	154	154	154
$z(\text{P–O})$	3.9	4.0	4.0	4.0	4.2
$r_1(\text{O–O})/\text{pm}$	251	250	248	252	252
$z(\text{O–O})$	4.5	4.7	4.3	3.8	4.5

PO_4 tetrahedra are linked to each other *via* two bridging oxygen atoms forming presumably non-straight chains.¹¹⁶ Cations are placed between the chains and are surrounded by different numbers of oxygen ions. One of the oxygen atoms in the tetrahedron is doubly bound to the phosphorus atom. However, the computational accuracy is not sufficient to differentiate bonds of phosphorus with bridging and terminal oxygen particles.¹¹⁶

The applicability of the ionic model to P_2O_5 is not obvious. The electronegativities of oxygen and phosphorus atoms (according to Pauling) are equal to 3.5 and 2.1, respectively. From their difference of 1.4, the degree of the P–O bond ionicity is only 39%, which is substantially lower than for silica (51%).

Computer models of non-crystalline P_2O_5 were constructed using the MD and CSR methods.¹¹⁷ The Born–Mayer pair potentials (1) with ion charges +5 and −2 were applied. The interaction parameters B_{12} and B_{22} were determined using the experimental data on $\text{Ca}(\text{PO}_3)_2$ (with $B_{11} = 0$). The $r_1(\text{P–O})$ was adjusted to 155 pm in a model of glassy oxide by varying the B_{12} parameter. The B_{22} parameter for the model of $\text{Ca}(\text{PO}_3)_2$ at 300 K was adjusted to reproduce the actual volume $8.40 \text{ cm}^3 (\text{g-ion})^{-1}$ (see Ref. 118). Models of glasses were obtained by rapid cooling from 2000 K to 0 K within the CSR method with a 2 pm step; one typical run included 500 iterations. In the simulation of cooling under isobaric conditions (P close to 0), both the $r_1(\text{P–O})$ distance and the volume of the system changed slightly (by 1–3 pm and 1%–3%, respectively). Therefore, the parameters were corrected and MD-relaxation at 2000 K followed by cooling to 0 K was performed again. This cycle was repeated until the calculated parameters conformed with the experimentally established values for $r_1(\text{Ca–O})$ and molar volume of $\text{Ca}(\text{PO}_3)_2$ glass. Finally, the values of $B_{12} = 1847.66$ eV and $B_{22} = 1009.98$ eV

were obtained. The latter is substantially less than that proposed for silicates (1500 eV).⁶⁵

The B_{ij} values found for $\text{Ca}(\text{PO}_3)_2$ oxide were used in order to construct models for P_2O_5 at 2000 K and 0 K using the MD and CSR methods. All models relaxed in 1000 steps at 6000 K (2.04 fs per step), then the system was cooled to 2000 K and annealed for two runs of 1000 steps each. A model of the glass at 0 K was obtained by switching from the MD to the CSR method (with 2 pm shifts) using models for liquid oxide after a molecular dynamic run of 1000 steps at 2000 K.

For the model of pure P_2O_5 at 2000 K and 0 K, the molar volumes were 46.2 and 45.6 $\text{cm}^3 \text{mol}^{-1}$, which is substantially less than the molar volume of the real glass (55.0 $\text{cm}^3 \text{mol}^{-1}$, see Ref. 118). In part, this discrepancy may be explained by a difference in the properties of real glasses prepared by different ways

—2 does not provide the dominant tetrahedral coordination of phosphorus particles in pure P_2O_5 . Better agreement with the experimental data may be achieved either by decreasing ion charges or taking into consideration three-particle interactions typical of covalent bonding. As it will be demonstrated below, the tetrahedral coordination of phosphorus ions in the glass may be obtained within the framework of the pair interaction by selecting lower effective ion charges.

7. Models of non-crystalline V_2O_5

The oxide V_2O_5 forms a glass upon ordinary cooling of the liquid. Glasses with the composition $\text{V}_2\text{O}_5 - (\text{Li}_2\text{O}, \text{Ag}_2\text{O}, \text{BaO}, \text{SiO}_2)$ were prepared by quenching between rotating cylinders.¹¹⁸

The structure of liquid V_2O_5 was studied by X-ray diffraction at 953 K and 1173 K.⁵¹ According to these data, the position of the first peaks in the PPCF at 1000 K for the V—V, V—O, and O—O pairs were at 345, 180, and 256 pm, respectively. The mean CN value of V—O was 5.2. The temperature practically did not affect the structure of the melt, and this is believed to be similar to the structure of a crystal built of zigzag chains of oxygen bipyramids with vanadium ion at the centre, which are linked to each other through remote oxygen ions into a continuous network.⁵¹ Addition of lithium, potassium, calcium, and lead oxides to V_2O_5 results in a decrease in the V—O distance (to 168 pm at 25 mol.% of PbO). However, the V—V, V—O, and O—O distances determined by X-ray and neutron diffraction of V_2O_5 were equal to 336, 170, and 276 pm, respectively, and CN of V—O pairs was 3.6.¹¹⁹ A model in which vanadium atoms occupy centres of VO_4 tetrahedra and every three vertices of the tetrahedron are common for neighbouring tetrahedra was suggested.¹¹⁹ In a liquid state, large clusters of tetrahedra have to decompose into constituents, and some vanadium atoms in the centres of tetrahedra may be substituted by oxygen atoms.

In a $\text{V}_2\text{O}_5 \cdot 4.4\text{TeO}_2$ glass, two V—O distances were found by neutron diffraction: 161 pm (CN 1.0) and 199 pm (CN 4.0).¹²⁰

The structure of liquid V_2O_5 was simulated.^{121–123} An MD-model of the oxide at 1050 K with the effective ion charges of +3.95 and –1.58 was described.¹²¹ The model contained 560 particles in the basic cube. The V—O distance was 178 pm, and CN for V—O was 6.1; the pressure of the system was ~30 GPa. A model of liquid oxide with the actual molar volume 78.4 $\text{cm}^3 \text{mol}^{-1}$ at 1000 K was constructed.¹²² The model contained 336 ions in the basic cube, ion charges were +5 and –2. The value of B_{12} (2970.0 eV) was determined from the lattice parameter of the crystalline oxide. For this model, the energy of the ionic V_2O_5 crystal appeared to be higher than the actual value (–38 314 kJ mol^{-1}) by ~13%. This difference is probably due to a significant contribution of covalent bonding in the real oxide. Besides, the model did not take into account van der Waals contributions to the total energy.

From the model, V—O distance was 180 pm, CN was 4.94, and the pressure was ~2 GPa. It was concluded that the structure of the V_2O_5 melts is loose and built up of oxygen bipyramids with vanadium ions in the centres and CN of V—O pairs close to 5.¹²² It was established that the CN distribution is rather narrow, and more than 92% of vanadium ions have five oxygen neighbours. The distribution of O—V—O azimuthal angles has an intense peak at 90° and a small peak at 155°. These angles are typical of a distorted trigonal bipyramid with the vanadium atom in the centre. Distribution of the Voronoi polyhedra also confirms the pyramidal structure.

A series of models for oxides with a general formula M_2O_5 was constructed using the potentials (1) at zero pressure.¹²³ The number of particles in all models was 497. For the model corresponding to V_2O_5 (with $B_{12} = 2970$ eV), the calculated energy was –33 160 kJ mol^{-1} at 2000 K and –33 390 kJ mol^{-1} at 1000 K (the difference between them is less than 0.4%).¹²² However, molar volumes for these models differed by 23% (62.3 and 78.4 $\text{cm}^3 \text{mol}^{-1}$, respectively). Checking with the use of the same programme demonstrated that each model is rather stable

Table 4. Distribution of CN for models of P_2O_5 at 2000 K.

CN	P—O (O—P)	O—O	CN	P—O (O—P)	O—O
1	(2)	—	6	18	96
2	(352)	—	7	—	165
3	(1)	1	8	—	65
4	19	—	9	—	23
5	105	3	10	—	2

(the transition from the MD to the CSR method implies an exclusively high cooling rate). Interionic distances for the P—P, P—O, and O—O pairs at 2000 K appeared to be equal to 313, 158, and 228 pm, respectively. The mean CN for P—O pairs was 4.99. Table 4 shows the distributions of CN in the model of P_2O_5 at 2000 K.

Similar results were obtained at 0 K. Distributions of CN for P—O pairs had a maximum at $z(\text{P—O}) = 5$. About 74% of phosphorus ions occupy centres of 5-vertex trigonal bipyramids, however a noticeable part of P^{5+} ions are surrounded by four or six O^{2-} ions (~13%–14% both). Virtually all O^{2-} ions in the P_2O_5 models have two P neighbours bridging PO_n groups. A bond group analysis indicate complete polymerisation of the structure.

Distribution of the O—P—O and P—O—P angles is as follows: $\theta(\text{O—P—O}) = 106.5 \pm 25.8^\circ$, $\theta(\text{P—O—P}) = 157.4 \pm 11.8^\circ$. Hence, the PO_5 bipyramids are linked through shared vertices, and the P—O—P angles are close to the Si—O—Si angles in silica.

The presence of a ring component of the structure was also analysed. A P—O pair with a distance between the ions less than 175 pm was considered as a link. In models of P_2O_5 at 2000 K and 0 K the 6- and 8-membered rings were found; and almost all particles of the model were included in the rings. The following topological parameters of P_2O_5 models at 2000 K were found: $\rho_1 = 0.931$ and $s = 1.51$. These values imply that the structure of P_2O_5 is rather loose and close in this sense to the structure of silica. According to these parameters, the tendency to glass formation also should be high, which is in agreement with the experimental data.

In the simulation of P_2O_5 at 0 K with the actual molar volume of 55.0 $\text{cm}^3 \text{mol}^{-1}$ by the CSR method, the interionic distances for the P—P, P—O, and O—O pairs were 323 pm, 161 pm, and 239 pm, respectively. The pressure was found to be about –30 GPa, CN of the P—O pairs decreased to 4.9, *i.e.* the tetrahedral configuration was still little represented (19% of the phosphorus ions). Distributions of azimuthal angles and topological parameters of the model were practically unchanged.

It is difficult to compare the real structure and the models of P_2O_5 at 2000 K due to the absence of experimental data. However, for amorphous P_2O_5 , the deviations from the real glass were significant; especially in CN of the P—O pairs. A model of ionic bonding with the use of the potential (1) with ion charges +5 and

during MD-relaxation for hundreds of steps (~ 1 ps). Thus, in this case two rather stable oxides with different prehistory and structures were found. Probably, this effect is analogous to the compacting of silica (by 10%–15% in volume), which had been reproduced earlier by MD method.⁹

Calculated^{122, 123} V–V, V–O, and O–O distances were 350, 180, and 257–259 pm, respectively. They are close to the experimental values⁵¹ but differ noticeably from the results of another study.¹¹⁹ The CN values for V–O pairs change from 4 to 6, where $\sim 70\%$ of vanadium ions have the CN = 5, and the mean CN is equal to 4.9–5.0.¹²³ For the models of liquid V_2O_5 , the values of topological parameters are as follows: $\rho_1 = 0.885$ and $s = 2.71$.¹²² Therefore, the structure of oxide is rather loose.

Taking into account the discrepancy in diffraction data, it is difficult to discuss the correctness of the models of vanadium pentoxide. A covalent component may give a substantial contribution to the interaction of particles in this oxide.

8. Models of non-crystalline WO_3

Diffraction data on the structure of non-crystalline tungsten oxides are scarce. For amorphous films of WO_3 , the electronographic study gave the values of W–W and W–O distances of 378 pm and 188 pm and the corresponding CN 5.7 ± 0.4 and 5.8 ± 0.2 .¹²⁴ A structure of bulk WO_3 glass was studied by anomalous X-ray scattering.¹²⁵ For the W–O pair two distances were found: 182 (W=O) and 220 pm (W–O); the mean distance is equal to 196 pm (CN 5.2). It was shown that for the O–O pairs the distance is 287 pm (CN 7.0) and for the W–W pairs, 372 pm (CN 4.2). Therefore, the results of the two studies^{124, 125} are in some disagreement. A study of $2Na_2O \cdot WO_3$ and $Na_2O \cdot 2WO_3$ glasses gave W–O distance close to 180 pm and CN 4.7 and 5.2, respectively.¹²⁶

The potential (1) with the parameters $B_{11} = 0$, $B_{22} = 1500$ eV, and $R_{ij} = 29$ pm was applied in models of liquid and amorphous WO_3 oxide composed of 500 ions.^{127, 128} The B_{12} parameter was determined provided the W–O distance was taken to be 180 pm, and was found to be 3400 eV. First, a CSR model at 0 K and zero pressure was constructed. Then the increases in temperature up to 2000 K were simulated by the MD method. After the relaxation, the system was cooled again to 0 K using the CSR method to check it for probable hysteresis effects. The molar volume of the amorphous oxide at 0 K was found to be equal to $28.7 \text{ cm}^3 \text{ mol}^{-1}$ and to $28.9 \text{ cm}^3 \text{ mol}^{-1}$ for the liquid one at 2000 K. The molar volume of the crystal at 300 K is $31.3\text{--}32.2 \text{ cm}^3 \text{ mol}^{-1}$ (see Ref. 129), which exceeds that of the amorphous oxide by 9%–12%. The reason for this effect is a rather loose structure of the crystal.

The adequacy of a purely ionic bonding approximation may be estimated for WO_3 . The atomisation energy of WO_3 was calculated using the Born–Haber cycle.¹³⁰ The sum of the first six ionisation potentials found in this way was 193.33 eV, and the actual sum is 193.7 eV. Therefore, the ionic bonding approximation is reasonable, and the higher ionisation energy of tungsten atoms is compensated by the Coulomb energy of ion interactions.

The mean thermal expansion coefficient for WO_3 models in the range of 0–2000 K is very small ($3.1 \times 10^{-6} \text{ K}^{-1}$). This is explained by the small ratio of the thermal energy at 2000 K to the total energy (0.0044). By the same reason, the low thermal expansion coefficient of SiO_2 (E_{kin}/E is 0.006) may be explained. Structure of WO_3 does not change substantially on heating, and the mean heat capacity is close to its classical limit $3R = 24.9 \text{ J(g-ion K)}^{-1}$.

The values of W–W, W–O, and O–O interionic distances were equal to 352, 179, and 238 pm at 2000 K and to 351, 179, and 236 pm at 0 K, respectively.¹²⁷ They very little depend on temperature. The W–O distance is in good agreement with the diffraction data. The first PPCF peak of the W–O pairs is isolated. The mean CN of the W–O pairs is 5.98; CN distributions of the W–O and O–W pairs were identical and rather narrow at 2000 K and 0 K.^{127, 128}

CN	1	2	3	4	5	6	7
Number of W ions	—	—	—	—	11	107	7
Number of O ions	4	371	—	—	—	—	—

Thus, $\sim 86\%$ of tungsten ions have 6 neighbouring oxygen atoms and are in the octahedral environment. Other tungsten atoms have 5 or 7 neighbours. Tetrahedral coordination was not observed in the models. This is at variance with the approximate structure interpretations.¹²⁶

It is noteworthy, that the content of W^{6+} ions with CN 6 in the WO_3 oxide is somewhat less than the content of Si^{4+} with CN 4 in silica (92%). Therefore, the first coordination sphere of W^{6+} ions is less rigid, due to the larger size of the tungsten ions and strong repulsion of the six surrounding O^{2-} ions.

The topological characteristics of WO_3 models are as follows:^{127, 128}

T/K	0	2000
ρ_1	0.979	0.972
s	1.55	1.42

The structure of the oxide is loose, but the values of ρ_1 are not very low. Pure WO_3 does not form glasses,¹¹⁸ but on sufficiently rapid cooling (quenching between rotating cylinders) it is possible to obtain a glassy oxide.¹³¹ Hence, the values of $\rho_1 = 0.97\text{--}0.98$ lie on the very limit of glass formation for the MO_3 oxides.

9. Models of non-crystalline Na_2O

Pure sodium oxide does not form glasses on cooling of a liquid. Diffraction data for sodium silicates have been reviewed.¹³² According to these data, the Na–O interionic distances at 300–1373 K are 233–240 pm and CN for the Na–O pairs lie in the range of 4–6. The molar volume of the liquid oxide at 1673 K is $33.0 \pm 4.6 \text{ cm}^3 \text{ mol}^{-1}$ (see Ref. 133).

Models of liquid and amorphous Na_2O were constructed with the pair potentials (1).^{103, 127, 134, 135} For the O–O pairs, the value of B_{22} was taken to be equal to 1500 eV, as for silicates. For the Na–Na pairs, the calculations gave $B_{11} = 842.2$ eV.^{10, 12} The B_{12} coefficient can be calculated from the molar volume of the crystalline oxide. Taking into account only two first terms in (1), the value of $B_{12} = 1601.9$ eV ($R_{ij} = 29$ pm) was obtained.^{103, 134} However, if the B_{11} value is chosen as 0, then $B_{12} = 1814.5$ eV. Since the interaction of the Na–Na pairs gives a small contribution to the energy, the value of $B_{11} = 0$ was chosen.¹²⁷

MD-models were constructed with account for Coulomb interactions according to Ewald–Hansen.³⁹ The molar volume of the non-crystalline oxide appeared to be equal to 27.6 to $28.6 \text{ cm}^3 \text{ mol}^{-1}$ at 0 K and $33.0\text{--}36.0 \text{ cm}^3 \text{ mol}^{-1}$ at 2000 K. Interpolation to 1673 K gives the value of $\sim 34.6 \text{ cm}^3 \text{ mol}^{-1}$, which is in good agreement with the experimental results. The Na–O distance is 222 pm at 0 K (see Ref. 134) and 228 pm at 2000 K.⁶⁴ In another study¹²⁷ the value of 222 pm was found at 2000 K. The deviations from $r_1(\text{Na–O})$ in silicates (233 to 240 pm) is reasonable, since this distance in a $Na_2O\text{--}SiO_2$ system increases with increase in the silica content.¹³⁴ The mean CN for the Na–O pairs is 2.9, which is less than the CN in the antifluorite crystal (4.0). This value is close to the lowest limit of the range of diffraction data for sodium silicates. The distribution of CN shows that only half of Na^+ ions have exactly four neighbours.

$z(\text{Na–O})$	3	4	5
Number of sodium ions	48	88	30

TPCF of the oxide contains only distinct first peaks attributed to the Na–O and Na–Na pairs, which precludes the interpretation of the structure from the diffraction data.¹³⁵

The topological characteristics of the Na_2O model at 0 K and 2000 K ($\rho_1 = 1.062$ and 1.018 , $s = 1.06$ and 1.01) show that the oxide has a rather dense structure in both amorphous and liquid states. The fact that the structure of amorphous oxide is dense explains the low tendency of Na_2O towards glass formation.

V. Simulation of homologous series of non-crystalline oxides

1. Models of non-crystalline oxides in the M_2O series

The description of oxides with a definite stoichiometry and using the potential (1) with B_{12} as the only variable parameter allows one to construct a series of models differing in the $r_1(M-O)$ interionic distances, which is equivalent to changes in the ion radius of the M ion. If real oxides are satisfactorily described by the potentials (1) with constant R_{ij} , B_{11} , and B_{22} , then the properties of the oxides can be calculated by an interpolation of data obtained for other members of the series. In that case, the efficiency of computational methods enhances substantially.

This idea was proposed in studies devoted to oxides of $2MO \cdot SiO_2$ series^{136–139} and then extended to other oxides. Two series of models for M_2O at 0 and 2000 K with the pair potentials (1) and the values of B_{12} ranging from 545.3 to 9999.0 eV, $B_{11} = 0$, $B_{22} = 1500$ eV, and $R_{ij} = 29$ pm, were considered.¹³⁵ Each model contained 249 ions. Estimates made from the molar volume of antifluorite-type crystals at $p = 0$ gave $B_{12} = 626.67$ eV for Li_2O , 3844.1 eV for K_2O , and 5320 eV for Rb_2O (the structure of Cs_2O is more complex). Coulomb interactions were taken into account by the Ewald–Hansen method.³⁹ The period of the basic cube was adjusted so that the pressure was close to zero. Due to fluctuations in the pressure, the molar volume of the models was determined with an error of 0.2%–0.3% at 0 K and 2%–4% at 2000 K.

Figure 3 shows the dependence of parameters of M_2O models on B_{12} at 2000 K. The adequacy of the potentials used can be checked by comparing the molar volumes for the models with the experimental data. An interpolation using the data from Fig. 3 for Li_2O with $B_{12} = 626.67$ eV gives the molar volume at 2000 K $7.9 \text{ cm}^3 (\text{g-ion})^{-1}$ and at 1673 K $7.75 \text{ cm}^3 (\text{g-ion})^{-1}$.¹³⁵ The actual value at 1673 K $[6.47 \pm 0.83 \text{ cm}^3 (\text{g-ion})^{-1}]$ (see Ref. 133) is less by 16%. For Na_2O at 2000 K the calculated molar volume was $12.0 \text{ cm}^3 (\text{g-ion})^{-1}$ at $B_{12} = 1601.94$ eV. The actual volume $11.0 \pm 1.5 \text{ cm}^3 (\text{g-ion})^{-1}$ at 1673 K (see Ref. 133) is close to the calculated value. For the K_2O model at 2000 K, the molar volume appeared to be equal to $15.5 \text{ cm}^3 (\text{g-ion})^{-1}$, which is also in accordance with the experimental value of $17.2 \pm 2.2 \text{ cm}^3 (\text{g-ion})^{-1}$ at 1673 K.¹³³ As it is clearly seen from Fig. 3, the $r_1(M-O)$ distance depends almost linearly on $\ln B_{12}$. The $r_1(M-M)$ and $r_1(O-O)$ distances depend monotonically on B_{12} .

Calculation of the TPCF for liquid oxides at 2000 K for X-rays showed that in the case of Li_2O , the M–M pairs do not contribute significantly due to a small scattering amplitude of Li atoms. For sodium and potassium oxides, the contribution of the M–M pairs is greater. The highest TPCF peak is due to the

M–O pairs. However, because of the mutual interference of the PPCF oscillations the corresponding TPCF are close to unity already at distances longer than 0.5 nm.

The mean CN for the M–O pairs also increase as B_{12} increases, i.e. with an increase in size of M^+ . In crystals, $z(M-O)$ is equal to 4, and melting or amorphisation is accompanied by a decrease in the CN of the M–O pairs. For the entire M_2O series, the range $2.6 < z(M-O) < 3.6$ is typical. Distributions of $z(M-O)$ become broader with the increase in B_{12} .

$z(M-O)$	2	3	4	5	6
Number of ions at					
$B_{12} = 545.3$	81	85	—	—	—
1601.9	48	88	30	—	—
3844.1	6	63	85	11	1
9999.0	8	71	76	10	1

For a broad distribution of CN, it is impossible to isolate any stable element of the structure, and the system should resemble more or less dense packing of spheres with different diameters. The broad distributions of O–M–O and M–O–M azimuthal angles also point to this fact.

Temperature only slightly affects the structure of the oxides. The $r_1(M-O)$ distances change insignificantly, but for the M–M and O–O pairs they increase noticeably with heating due to the thermal expansion. The ratio of molar volumes $V_{2000 \text{ K}}/V_{0 \text{ K}}$ for $B_{12} = 545.3$ eV is equal to 1.08 (for Li_2O), 1.16 (for Na_2O), and 1.12 (for K_2O). An important role of the temperature is due to the fact that E_{kin} at 2000 K makes a noticeable part of E (from 2.6% for Na_2O up to 4.1% for K_2O).

The topological coefficient ρ_1 increases from 0.95 to 1.06 as B_{12} increases (see Fig. 3), while the s coefficient decreases from 1.17 to 1.00. Therefore, structures of the oxides with $B_{12} > 1600$ eV (including Na_2O , K_2O , Rb_2O) are close to the dense one. That is why it is difficult to prepare these compounds in a glass state.

If M–O distance in non-crystalline M_2O oxides is suggested to be equal to the sum of ion radii and usual values are taken for M^+ ions (viz., 68 pm for Li^+ , 98 pm for Na^+ , 133 pm for K^+ , and 149 pm for Rb^+), then the radius of O^{2-} appeared to be 118 ± 7.7 pm, which is in agreement with the estimates of its crystallographic radius on the fluoride scale (121–128 pm).¹⁴⁰ Thus the approximate value of the radius is 120 pm.

Analysis of the thermodynamic properties of the oxide models was performed.¹³⁵ Comparison of experimental values for total energy of M_2O crystals with the results of simulations at $B_{11} = 0$ and $B_{22} = 1500$ eV (taking account of only Coulomb interactions and electron shell repulsion) demonstrated that the difference is 12% for Li_2O and gradually decreases to 4% for Cs_2O .

Oxide	Li_2O	Na_2O	K_2O	Rb_2O	Cs_2O
$-E(\text{calc.})/\text{kJ} (\text{g-ion})^{-1}$	1020.1	852.9	770.5	740.2	695.7
$-E(\text{exp.})/\text{kJ} (\text{g-ion})^{-1}$	910.8	788.2	738.0	692.4	667.4

The deviations are probably caused by the fact that the R_{M-O} parameter for light ions differs from the conventional value of 29 pm. In principle, the agreement between the experimental and simulated results may be improved by adjusting the R_{ij} values specifically for each oxide. A contribution of covalent interactions to the potential, which decreases for heavier Group I cations and which was not taken into account in the simulation, may be another reason for the deviations.

Amorphisation energies ΔE_{am} for the models decrease from $40 \text{ kJ} (\text{g-ion})^{-1}$ for Li_2O to $14 \text{ kJ} (\text{g-ion})^{-1}$ for Cs_2O (see Ref. 135). Heats of melting [from $19.7 \text{ kJ} (\text{g-ion})^{-1}$ to $6.4 \text{ kJ} (\text{g-ion})^{-1}$] are 1.6–3.4-fold less than ΔE_{am} and also gradually decrease as B_{12} increases. The ratio of volumes of amorphous and crystalline phases also changes analogously. Amorphisation of a model of a Li_2O crystal at 0 K is accompanied by an increase in the volume by 34%, and for model of Cs_2O by 4%. These features of amorphisation are due to structural changes. Amorphisation of Cs_2O is accompanied by a decrease

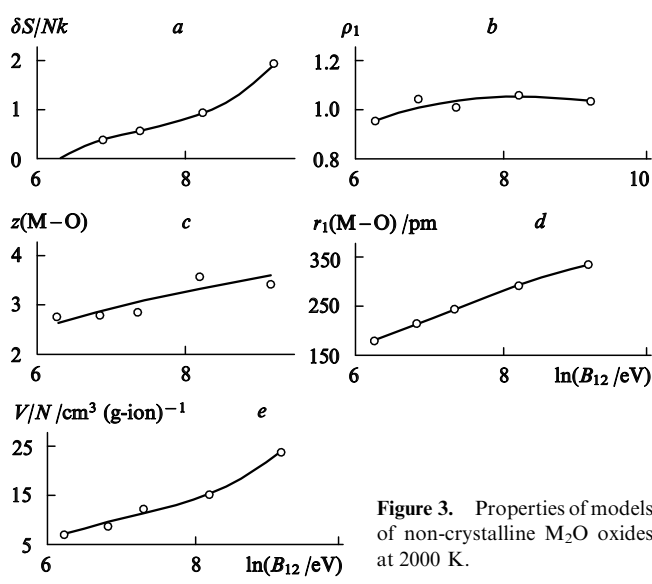


Figure 3. Properties of models of non-crystalline M_2O oxides at 2000 K.

in the mean CN for the M–O pairs from 4 to 3.6; for Li₂O, the CN for the M–O pairs decreases to 2.5.

The change in the Gibbs energy along the homologous series may be calculated using the expression¹³⁸

$$\delta G_y = \int_{y_1}^{y_2} \langle U_{12} \rangle dy, \quad (11)$$

where $y = \ln(B_{12})$, y_1 and y_2 refer to the initial and final states, $\langle U_{12} \rangle$ is the mean equilibrium value of energy of electron shell repulsion of the M–O pairs. In (11), the integration is performed at constant pressure and temperature. Using the values of $\langle U_{12} \rangle$ obtained from the molecular dynamic experiments, the value of δG_y may be calculated. Further, taking into account that $\delta G = \delta E + p\delta V - T\delta S$, the change in entropy δS for each member of the series may be determined. The change in $\delta S/Nk$ is shown in Fig. 3: as B_{12} increases, the configurational entropy of the oxide (at a constant mass of M^+ ion) increases monotonically, *i.e.* gradual disordering of the structure takes place, which is manifested particularly in the broadening of CN distributions. The maximum change in entropy for the system considered is $\sim 2Nk$.

The term δS_y represents only the configurational part of the change in entropy. If the mass of m_i ion is changed to m_j on going from one oxide to another, then the contribution

$$\delta S_m = \frac{3}{2}NkX_M \ln(m_j m_i^{-1}),$$

has to be added to the value of δS_y , where $X_M = 2/3$ is the ionic contribution of the M^+ ion.

2. Models of non-crystalline oxides in the MO series

MO series includes such important components of industrial slags and glasses as MgO, CaO, SrO, BaO, and probably BeO, FeO, MnO, PbO, *etc.* The first model of CaO composed of 216 ions was constructed using MD and CSR methods with the pair potentials (1) and the following parameters: $B_{11} = 0$, $B_{12} = 3283$, $B_{22} = 1500$ eV, and $R_{ij} = 29$ pm.⁶⁵ The value of B_{22} was adjusted so as the O–O distance in the models of calcium and iron silicates was close to the values determined by diffraction methods (~ 323 pm, see Ref. 141). For the Ca–O pairs, the parameter $B_{12} = 3283$ eV was from the density of crystalline CaO. The electrostatic energy appeared to be -4037 kJ mol⁻¹, and the energy of electron shell repulsion was 483 kJ mol⁻¹. The total energy (not accounting for zero vibrations) was equal to -3554 kJ mol⁻¹, which is in reasonable agreement with the experimental value⁶⁵ of the energy of the crystal (-3378 kJ mol⁻¹); the difference being 5.2%. The modulus of bulk compressibility was 171 GPa compared to the experimental value of 115 GPa. Therefore, the Born–Meyer potentials are not quite precise, but they can be used for construction of models.

An investigation of models of non-crystalline MO oxides (composed of 216 ions) was performed.^{103,142} The Coulomb interactions were taken into account using the Ewald–Hansen method.³⁹ The models with $B_{12} = 400$ –800 eV describe hypothetical oxides with very small M^{2+} ions. Models corresponding

to MgO, FeO, CaO, SrO, and BaO have B_{12} equal to 1441.4, 1900.0, 3283.0, 4744.1, and 8885.1 eV, respectively. The B_{12} values were determined from the experimental lattice parameters. The calculated values of energy of the crystals using the Born–Meyer potential was lower than corresponding experimental values by 2.2%–5.8%. This difference indicates a certain inaccuracy of the potentials (1).

A model of amorphous phase at 0 K was constructed using the MD method starting from a random initial state.^{103,142} Then the temperature was increased up to 2000 K by the MD method and the system was relaxed during several hundreds steps to reach the equilibrium state. Some models were constructed with the use of the previous ones with other B_{12} values. The amorphisation energies [45 – 65 kJ (g-ion)⁻¹] were calculated as differences between energies of the amorphous phase and the crystal. Their ratios to the heats of melting of the corresponding oxides increased from 1.18 to 1.84 on going from MgO to BaO. The amorphisation was accompanied by a substantial increase in a volume of crystal (by 17% for BaO and 38% for MgO).

Dependencies of V/N , $r_1(ij)$, mean CN $z(M-O)$, ρ_1 , and $\delta S/Nk$ on B_{12} are shown in Fig. 4. An increase in B_{12} results in a monotonic increase in the M–M and M–O distances, while the O–O distance changes non-monotonically. The volume of oxides passes through a minimum at $B_{12} = 800$ –1900 eV.

The reason for the appearance of the minimum can be understood when the change in the CN of M–O pairs is considered. As it is seen from Fig. 4, if $B_{12} \leq 500$ eV then CN equals 2 and the system has a chain structure. The O–M–O and M–O–M azimuthal angles at 2000 K are close to 160° and correspond to the zigzag –M–O–M–O– arrangement of the ions. Analysis of distribution of CN demonstrated that when $B_{12} \leq 500$, virtually all M^{2+} ions have two neighbours (O^{2-} ions) and vice versa. The distance $r_1(M-O)$ is 110–120 pm. In the case of M^{2+} ion with the smallest size (Be), the distance is 180 pm in the crystal and 151 pm in the amorphous oxide. Therefore, models with $B_{12} \leq 500$ eV are hypothetical.

An abrupt decrease in the molar volume when the value of B_{12} approaches 800 eV is caused by a rapid increase in the CN of the M–O pairs from 2 to 3. When CN is 3, a layered trigonal structure appears. The O–M–O and M–O–M angles are 108 – 112° , *i.e.* the closest neighbours of M(or O) ions occupy vertices of strongly flattened trigonal pyramids. The contribution of ions with $z(M-O) = 2$ or 4 is relatively small ($< 30\%$), thus oxides with $B_{12} = 800$ eV have rather ordered structures.

The transition to $B_{12} \geq 1900$ eV results in a substantial broadening of distribution of CN for the M–O pairs, and the mean CN approaches the value of 6, typical of the MO crystal lattice. In the range of $B_{12} = 1441$ –1900 eV, the CN is almost constant [$z(M-O) = 4.14$ – 4.90], and consequently the molar volume changes only slightly. This is probably due to the high stability of the structure with $z = 4$ and a tetrahedral coordination of ions. However, this coordination is observed only as a mean value since the distributions of CN $z(M-O)$ in MgO and FeO models are rather broad.

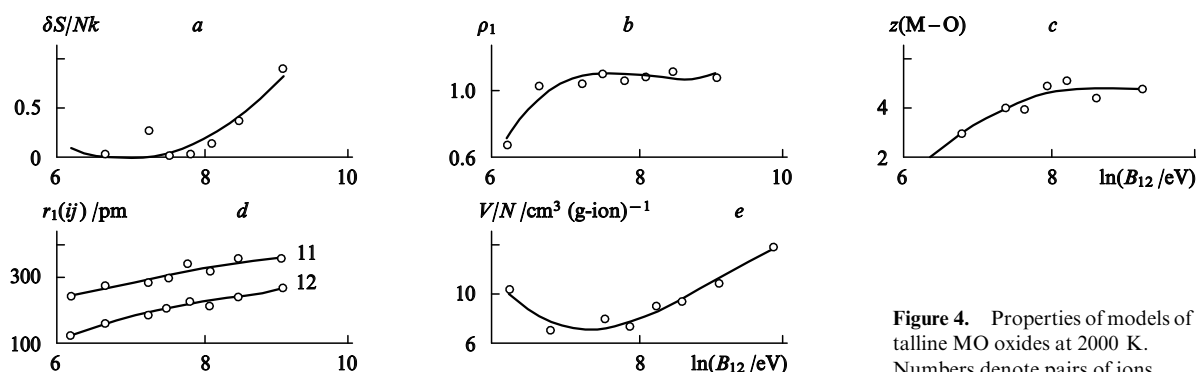


Figure 4. Properties of models of non-crystalline MO oxides at 2000 K. Numbers denote pairs of ions.

$z(\text{M}-\text{O})$	3	4	5	6	7
Number of M ions					
for a model of MgO	12	74	22	—	—
for a model of FeO	1	26	61	19	1

Temperature affects the structure of oxides relatively little, since even at 2000 K the thermal energy is only 1.0%–1.7% of the total energy. The mean heat capacity for all models [19.8–26.6 J (g-ion K)^{−1}] is close to the classical value $3R = 24.9$ J (g-ion K)^{−1}.

The value of the topological parameter ρ_1 is low for models with $B_{12} \leq 800$ eV (see Fig. 4), *i.e.*, the corresponding structures are rather loose. The s parameter is 2.68 for $B_{12} = 500$ eV and even 4.00 for $B_{12} = 400$ eV. However, the MgO model already has a quite dense structure ($\rho_1 = 1.04$ at 2000 K and 1.05 at 0 K). Other models have $\rho_1 = 1.07$ –1.08 and $s = 1.00$ –1.07. These structures are topologically dense, which accounts for the difficulty in obtaining the real MO oxides in a glassy state.

The properties of models with $B_{12} \leq 800$ eV vary with a substantial hysteresis.¹⁴² A model constructed with $B_{12} = 500$ eV from a random initial state by the CSR method gave a molar volume of only 5.85 cm³ (g-ion)^{−1} and an energy of −2394.4 kJ (g-ion)^{−1}. Its annealing (2000 K) is accompanied by an increase in the volume up to 11.2 cm³ (g-ion)^{−1}. For simulation of this process, more than 1000 steps of the MD method were required. After cooling to 0 K using the CSR method and subsequent relaxation, the volume was equal to 11.4 cm³ (g-ion)^{−1}. The energy of this state is 18.3 kJ (g-ion)^{−1} lower than that of the initial state. At higher B_{12} values, the hysteresis effects are almost unnoticeable. They are typical of loose structures and their nature is similar to the processes that occur in the compacting of silica.

Changes in the Gibbs energies and entropies on moving along the MO series were calculated as for M₂O.¹⁴² This required that the integration of repulsion energies $\langle U_{12} \rangle$ was performed according to the equation (11). It was demonstrated, that the configurational entropy of oxides at 2000 K virtually does not change in the range $500 \leq B_{12} \leq 2550$ eV and begins to increase when $B_{12} > 2550$ eV. This growth is caused by broadening of distributions of CN and azimuthal angles and by the increase in the degree of disordering on going from loose to the topologically dense systems.

3. Models of non-crystalline oxides in the M₂O₃ series

A series of models for amorphous and liquid M₂O₃ oxides was constructed with the potentials (1) and parameters $B_{12} = 580$ –5000 eV. The value of 800.0 eV corresponds to boron oxide, 1479.86 to Al₂O₃, 2114.2 and 2453 to Fe₂O₃; other models correspond to hypothetical oxides. Data for the three above-mentioned compounds have already been discussed. A collapse in this series occurs when $B_{12}^{\text{cr}} = 550$ eV; the lowest value of 580 eV only slightly exceeds the critical one.

All models contained 500 ions in the basic cube. The edge length of the basic cube was selected so as to give the pressure close to zero. Fig. 5 shows the characteristics of the models in the M₂O₃ series at 2000 K. The $r_1(\text{M}-\text{M})$ and $r_1(\text{M}-\text{O})$ distances depend

almost linearly on $\ln B_{12}$. The molar volume of the oxide has a deep minimum at $B_{12} \simeq 1480$ eV. The first members of the series have the mean values of CN equal to 3. This value increases monotonically up to ~ 5.9 when $B_{12} = 5000$ eV. As in the case of the MO series, the minimum of the molar volume is due to a rapid increase in the CN and a rearrangement of the structure in the range 1150–1480 eV.

Distributions of CN for the M–O and O–M pairs are the most narrow when $B_{12} = 590$ and 800 eV and rapidly broaden at larger B_{12} values. Boron oxide is the most ordered in the configurational sense. The value of $z(\text{M}-\text{O}) = 4$ can be obtained for an oxide with $B_{12} = 1195$ eV. In such an oxide, the values of $z(\text{O}-\text{M})$ equal to 2 and 3 have to occur in the ratio 1:2, which does not allow one to provide as good ordering of the oxygen subsystem as in boron oxide, where $z(\text{O}-\text{M}) = 2.00$.

Data on CN are confirmed by the character of the distributions of azimuthal angles. At 2000 K, these distributions are as follows:

B_{12} / eV	$\theta(\text{O}-\text{M}-\text{O})$ / deg	$\theta(\text{M}-\text{O}-\text{M})$ / deg
580	121.7 ± 14.9	160.1 ± 10.1
800	119.3 ± 10.2	153.2 ± 19.2
1480	106.9 ± 23.3	121.1 ± 18.6
2453	105.4 ± 26.9	113.1 ± 19.6
5000	98.8 ± 28.0	108.4 ± 23.5

The O–M–O angle approaches 90° at higher B_{12} values, which roughly corresponds to an octahedral packing of the closest neighbours. In this case, $z(\text{M}-\text{O}) \simeq 6$ and $z(\text{O}-\text{M}) \simeq 4$, *i.e.* the surrounding of the oxygen atom by the metal atoms is almost tetrahedral. This is in keeping with the mean M–O–M angle (109°), which is therefore close to that of the ideal tetrahedron.

Taking into account that the effective radius of the O^{2−} ion for non-crystalline oxides is ~ 120 pm (see above), the radii of the M³⁺ ions can be calculated for B_{12} from the plot of $r_1(\text{M}-\text{O})$ depicted in Fig. 5. The model with $B_{12} = 3500$ eV corresponds to the oxide with the ionic radius of 92 pm. The radii of Y³⁺ and Ti³⁺ ions (93 and 95 pm, respectively) are close to this value. A system with $B_{12} = 5000$ eV corresponds to an ion with a radius of 108 pm, which is close to the radius of La³⁺ (115 pm). Further increase in B_{12} results in a region of unreal hypothetical large cations.

The topological characteristics (ρ_1 and s) in the M₂O₃ series indicate a noticeable looseness of the models with $B_{12} = 580$ eV (0.695 and 3.50, respectively) and with 800 eV (0.787 and 2.34). Nevertheless, the model of Al₂O₃ is almost dense ($\rho_1 = 1.056$ and $s = 1.16$). On further movement along the series the structure of oxides remains topologically dense.

The changes in the configurational Gibbs energy and entropy were calculated for the M₂O₃ series according to the equation (11). Dependence of $\delta S/Nk$ on B_{12} is shown in Fig. 5. When $B_{12} > 2453$ eV, the entropy is virtually constant and $\delta S_y = 9.6 \pm 0.9$ J (g-ion K)^{−1}. A decrease in B_{12} to 800 eV and transition to a more ordered layered structure of boron oxide is accompanied by a decrease in the configurational entropy. Further decrease in B_{12} results in a slight increase in the entropy due to

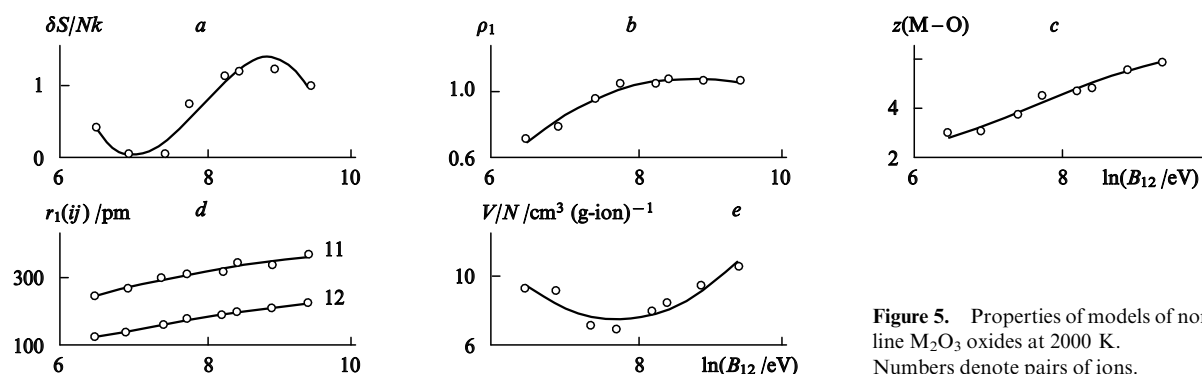


Figure 5. Properties of models of non-crystalline M₂O₃ oxides at 2000 K. Numbers denote pairs of ions.

greater disorder because of the broadening of CN distributions mentioned above.

4. Models of non-crystalline oxides in the MO₂ series

Non-crystalline oxides of the MO₂ series include silica and a glass-forming GeO₂ oxide. It is also possible to obtain glassy TeO₂ by quenching it between rotating cylinders.¹³¹ Such oxides as TiO₂, SnO₂, and ZrO₂ do not form glasses on ordinary cooling of a liquid.¹⁴³

Glassy SiO₂ and GeO₂ have been intensely studied by diffraction methods. The $r_1(ij)$ distances for GeO₂ were determined using anomalous X-ray scattering: $r_1(\text{Ge}-\text{Ge}) = 310-320$ pm, $r_1(\text{Ge}-\text{O}) = 160$ pm, $r_1(\text{O}-\text{O}) = 280$ pm.¹⁴⁴ The following r_1 distances for glassy GeO₂ were reported:¹⁴³ 315–345 pm for Ge–Ge pairs, 170–174 pm for the Ge–O pairs, and 283–285 pm for the O–O pairs. The mean CN for the Ge–O pairs lies in the range of 3.9–4.0. The mean Ge–O–Ge azimuthal angle is 133° (see Ref. 145). In an Na₂O·4GeO₂ glass, the Ge–O distance is 180 pm.¹⁴⁶ For pure TeO₂, no diffraction data were found. For a glass of composition V₂O₅·9TeO₂, neutron diffraction gave the Te–O distances of 192 pm ($z = 2.71$) and 216 pm ($z = 0.85$ pm).¹²⁰ In a SiO₂–TiO₂ glass (< 10 mol.% of TiO₂), the Ti–O distance appeared to be equal to 189–191 pm.¹⁴⁶

Models for MO₂ oxides composed of 498 ions in the basic cube were constructed using the MD and CSR methods at 0 K and 2000 K.⁵³ The pair potentials (1) were applied with the following parameters: $Z_1 = +4$, $Z_2 = -2$, $B_{11} = 0$, $B_{22} = 1500$ eV, $R_{ij} = 29$ pm. Since for this series $B_{12}^{\text{tr}} = 734$ eV, the values of B_{12} were chosen in the range of 850–8000 eV; the values $B_{12} = 1729.5$ eV and 1848 eV were proposed for silica and for simulations of the Si–O pairs in silicates, respectively.⁸⁴

Figure 6 shows the characteristics of MO₂ models as the function of B_{12} . The distance of $r_1(\text{M}-\text{O})$ depends linearly on $\ln B_{12}$. The M–M and O–O distances also increase with increase in B_{12} . When $B_{12} = 850$ eV, $z(\text{M}-\text{O}) = 3.70$. Extrapolation of the curve in Fig. 6c to the stability limit gave $z(\text{M}-\text{O}) = 3.5$, i.e. CN of 3 and 4 are equiprobable.

Distributions of CN for the M–O pairs in the models have the following form:

$z(\text{M}-\text{O})$	3	4	5	6	7	8	9	Mean CN
Number of M ⁴⁺ ions								
at $B_{12} = 850.0$	50	116	—	—	—	—	—	3.70
1729.5	7	152	7	—	—	—	—	4.00
3500.0	—	12	58	80	15	1	—	5.61
8000.0	—	—	1	47	86	30	1	6.91

The increase in B_{12} (i.e. the increase in the size of an M⁺ ion) is accompanied by an increase in the mean CN for the M–O pairs and broadening of its distribution. The MO₂ structure rearranges in the range $750 < B_{12} < 1000$ eV, when the trigonal structural elements are replaced by tetrahedral ones. A small minimum of the molar volume near $B_{12} = 1250$ eV (see Fig. 6e) is due to the rearrangement. A similar process is typical of oxides of the MO series in the range $800 < B_{12} < 1440$ eV (see above).

The next rearrangement of the structure occurs in the range $2000 < B_{12} < 3000$ eV. Here, $z(\text{M}-\text{O})$ increases abruptly up to 6 (see Fig. 6c), the distribution of $z(\text{M}-\text{O})$ becomes substantially broader, and the elements of the tetrahedral networks typical of silica disappear. Further increase in B_{12} does not lead to any new structural rearrangement.

These results agree with the results of analysis of the azimuthal angle distribution. When $B_{12} \leq 1848$ eV, the mean O–M–O angle is close to the tetrahedral one, and the $\theta(\text{M}-\text{O}-\text{M})$ angle is 156–160°. Similar distributions were obtained for silica (see above). Further increase in B_{12} is accompanied by a decrease in the mean value of O–M–O and M–O–M angles, but their distributions broaden by a factor of 2–3. The values of topological parameters ρ_1 (see Fig. 6b) and s indicate that the structures of oxides in the MO₂ series are loose when $B_{12} < 3500$ eV and close to the dense one when $B_{12} \geq 5000$ eV.

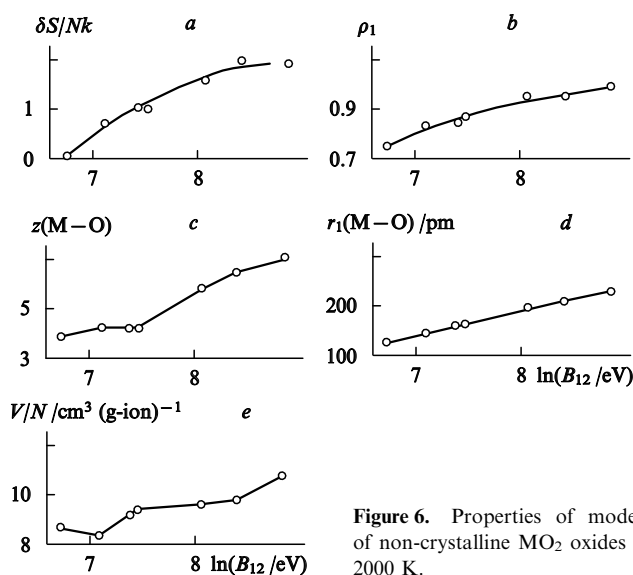


Figure 6. Properties of models of non-crystalline MO₂ oxides at 2000 K.

Comparison of the models with the real oxides in respect of $r_1(\text{M}-\text{O})$ distances and M⁴⁺ ion radii was performed.⁵³ Oxides with $B_{12} < 1700$ eV are hypothetical. The value of $B_{12} = 2080$ eV corresponds to GeO₂, 2940 eV to TiO₂, and 3410 eV, to TeO₂. A model with $B_{12} \approx 3500$ eV corresponds to ZrO₂ and with, $B_{12} \approx 5000$ eV to UO₂. An intermediate value (between 5000 and 8000 but closer to 5000 eV) corresponds to CeO₂.

An increase in temperature from 0 to 2000 K affects insignificantly the structure of the models. Positions of TPCF peaks do not virtually shift and their heights decrease only slightly. Coordination numbers for the M–O pairs also insignificantly depend on temperature. This is due to the fact that even at 2000 K the thermal energy of the oxides is very small compared to their total energy (0.5%–0.7%). The thermal expansion coefficient is also very small and almost equal to zero when $B_{12} = 8000$ eV.

The changes in the Gibbs energy and entropy along the MO₂ series were calculated⁵³ using the equation (11). The magnitude of $\delta S/Nk$ increases monotonically as in the M₂O and MO series (see Fig. 6a).

The relation between the topological looseness of oxide structures and their tendency to glass formation has been discussed above. Since SiO₂ and GeO₂ readily form glasses on ordinary cooling of a liquid, and TiO₂, SnO₂, and ZrO₂ do not form glasses, the value $B_{12} \approx 2500$ eV may be selected as the limit of glass formation. The $\rho_1 = 0.92$ and $s \approx 1.25$ coefficients correspond to this point. An estimate of ρ_1 from the plot (see Fig. 6b) for TeO₂ gives $\rho_1 = 0.94$ at $B_{12} \approx 3410$ eV, which only slightly exceeds this limit (0.92). This is in accordance with the fact that pure TeO₂ does not form a glass on ordinary cooling of a liquid but does form it on quenching between rotating cylinders.

5. Models of non-crystalline oxides in the M₂O₅ series

Non-crystalline oxides of the M₂O₅ series include such compounds as P₂O₅ and V₂O₅ along with As₂O₅, Nb₂O₅, Ta₂O₅, etc. Among these oxides, only P₂O₅ and V₂O₅ form glasses on ordinary cooling of a liquid, and niobium and tantalum oxides do not form glasses even on quenching between rotating cylinders.¹³¹ The properties of P₂O₅ and V₂O₅ models were described above. There are very few diffraction data on the structures of melts and glasses containing M₂O₅ oxides. The structure of an Nb₂O₅·2B₂O₃·2K₂O glass was studied by XRD; the values of 190, 311, 317, and 385 pm were obtained for the Nb–O, Nb–B, O–O, and Nb–Nb distances, respectively.¹⁴⁷ The mean CN for the Nb–O pairs is ~ 6.0 . The structure of the oxide contains a network of cyclic elements with six- and four-membered groups, such as NbO₆, BO₃, and BO₄.¹⁴⁷

Thus, the data on the structure of non-crystalline oxides of this series are quite fragmentary. There have been only a few studies on their thermodynamic properties. The Physicochemical properties of the non-crystalline M_2O_5 oxides were studied¹²³ using MD method. The potentials (1) were used with the following parameters: $Z_1 = +5$, $Z_2 = -2$, $B_{11} = 0$, $B_{22} = 1500$ eV, and $R_{ij} = 29$ pm. The dipole-dipole and dipole-quadrupole interactions were not taken into account. The critical value $B_{12}^c = 918$ eV, so the models were constructed for the range of $B_{12} = 950$ – 8000 eV.¹²³ Spherically symmetrical potentials provide the equivalence of all M–O bonds, which is typical of non-crystalline oxides. Each model comprised 497 ions. The Coulomb interactions were taken into account using the Ewald–Hansen method.³⁹ The edge length parameter of the basic cube was adjusted to maintain the pressure close to zero.

In order to examine the presence of hysteresis phenomena in the oxides, after heating of the system up to 2000 K its cooling to 0 K was simulated. The calculated energy appeared to be somewhat lower than the corresponding value for the initial models constructed using the CSR method (by $\sim 0.5\%$). It was shown that temperature insignificantly affects the properties of the oxide models. At zero pressure, the volume of the system increases by not more than 2% when the temperature changes from 0 K to 2000 K. In this respect, M_2O_5 oxides are similar to the MO_2 oxides. Positions of the TPCF peaks do not shift when the temperature is increased but the peaks become broader and less intense. The values of CN for the M–O pairs also change only slightly, as well as the position of the centres and widths of the O–M–O and M–O–M azimuthal angle distributions. The thermal energy is only 0.4%–0.6% of the total energy.

Figure 7 shows the dependences of the simulated characteristics for M_2O_5 oxides on B_{12} . The molar volume has a deep minimum at $B_{12} = 1500$ eV. The mean CN for the M–O pairs increases from 3.6–4.0 at $B_{12} = 950$ eV to 7.4–7.9 at $B_{12} = 8000$ eV. Such changes of the characteristics indicate a substantial structural rearrangement in the range of B_{12} values from 950 eV to 2500 eV. The structure of the first oxide ($B_{12} = 950$ eV) is intermediate between continuous random network with $z(M-O) = 4$ and layered trigonal [$z(M-O) = 3$] structures. Distributions of $z(M-O)$ in the M_2O_5 oxides are as follows:

$z(M-O)$	3	4	5	6	7	8	9	10
Number of M^{4+} ions								
at $B_{12} = 950$	59	83	—	—	—	—	—	—
1500	—	76	63	3	—	—	—	—
2500	—	20	98	24	—	—	—	—
3500	—	11	93	38	—	—	—	—
5000	—	—	24	76	36	5	1	—
8000	—	—	—	17	61	49	14	1

When $1500 \leq B_{12} \leq 3500$ eV, the distributions of $z(M-O)$ are limited by 4–6, but at $B_{12} \geq 5000$ eV their distribution becomes noticeably broader and shifts towards the greater values. A trigonal bipyramid with $z(M-O) = 5$ dominates as a structural element only in the range of B_{12} values from 2500 eV to 3500 eV.

Comparison of the models constructed with the real M_2O_5 oxides can be performed by the analysis of the $r_1(M-O)$ distances. For liquid V_2O_5 , this distance is close to 180 pm. The curve on Fig 7d allows one to estimate the value of B_{12} as ~ 2980 eV. An estimate made from the density of the crystal at 0 K and $p = 0$ gives a close value (2970 eV). A radius of 120 pm may be taken for O^{2-} ion. In this case, the difference $r_+ = r_1(M-O) - 120$ pm indicates that B_{12} is ~ 1800 eV for P_2O_5 , 2400 for As_2O_5 , 3360 for Sb_2O_5 , 3940 for Nb_2O_5 , 3940 for Ta_2O_5 , and 4230 eV for Bi_2O_5 . Therefore, the range of B_{12} from 1800 to 4230 eV corresponds to the real M_2O_5 oxides. And consequently, models with $B_{12} \leq 1500$ or $B_{12} \geq 5000$ eV are hypothetical. For models of real oxides, the distributions of $z(M-O)$ are such that the ordering type can not be described by an alternation of certain elements, a like trigonal bipyramid or an octahedron as it was suggested for V_2O_5 .⁵¹ An

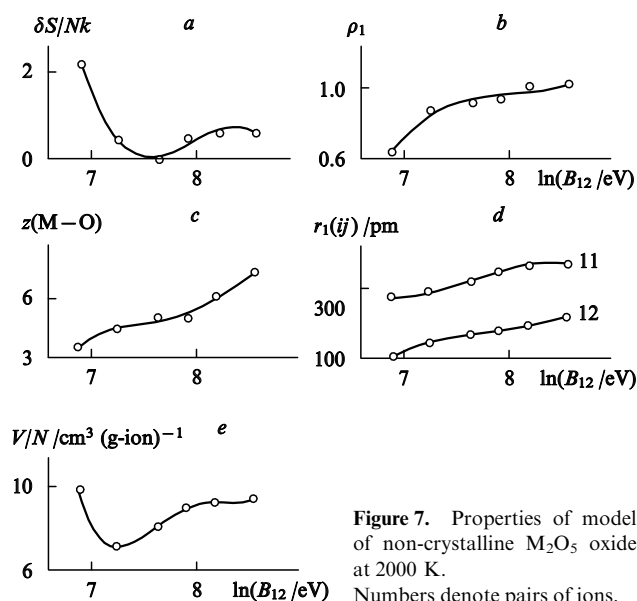


Figure 7. Properties of models of non-crystalline M_2O_5 oxides at 2000 K. Numbers denote pairs of ions.

oxide with $B_{12} = 2500$ eV (the closest real oxide is As_2O_5) occupies the best position: for this oxide the distribution is almost symmetrical relative to $z(M-O) = 5\%$ and 69% of M^{5+} ions have exactly five O^{2-} neighbours.

It should be kept in mind that distributions of CN of the M–O pairs in real oxides may be more narrow than in the corresponding models. In general, relatively small models of non-crystalline substances composed of several hundreds or thousands particles contain more ‘defects’ per atom than the real substances. This fact has been established for amorphous silicon and germanium but it also holds for other oxides. The reason for the higher defectiveness is boundary conditions in the basic cube. Presumably, the same reason causes very slow (compared to the real oxide) decrease in the self-diffusion coefficients in the models on cooling.

According to the values of ρ_1 , all M_2O_5 oxides have loose structures, especially in the cases when $B_{12} < 5000$ eV (see Fig. 7b). This is typical of all real M_2O_5 oxides. The reason for the looseness is presumably the unfavourable stoichiometry (seven atoms per molecule), which cannot exist in more or less regular networks.

Substantial complication of the oxide structures with an increase in B_{12} is accompanied by a small decrease in the mean value of the O–M–O azimuthal angle (from 110 to 100°). However, the width of distribution of this angle increases from 18 to 31°. The value of M–O–M angle changes along the series much more strongly (from 165 to 116°), and the distribution width is doubled. In well-ordered network structures of B_2O_3 and SiO_2 , the widths of angle distributions obtained in computer simulations were usually 8–10°. This feature also does not permit reliable conclusions on the presence of distinct structural elements in M_2O_5 oxides.

The looseness of structures is clearly seen in the visual study of spatial models constructed from balls of different diameters with the coordinates taken from the results of computer simulations of the oxides. For instance, large irregular pores situated between such groups as MO_4 , MO_5 , or MO_6 linked through shared vertices, can be seen in a spatial model built based on a calculation for $B_{12} = 2500$ eV. The surface of the pores is formed by oxygen ions and their repulsion stabilises the shape of pores. The packing of O^{2-} ions does not contain any linear or layered elements.

The maximum pore size was 163 pm, i.e. a positive ion or a neutral atom of a relatively large size may easily occupy the pore. In the model, six pores with radii > 140 pm, six pores with radii between 130 and 140 pm, etc. were found. These results, in particular, allow one to estimate the solubility of noble gases in

the oxides. An analysis of bound groups showed that all M_2O_5 oxides are completely polymerised (in terms of the polymer theory of slags).

According to Fig. 7b, for V_2O_5 with $B_{12} = 2970$ eV, $\rho_1 \approx 0.96$, and for Nb_2O_5 and Ta_2O_5 with $B_{12} = 3940$ eV, $\rho_1 \approx 1.00$. Thus, the glass formation limit for the M_2O_5 oxides lies in the range $0.96 < \rho_1 < 1.00$ ($\rho_1 \approx 0.97$) that is slightly higher than for the MO_2 oxides. This shift is due to a more complex structure of the M_2O_5 oxides. Therefore, P_2O_5 , V_2O_5 , As_2O_5 , and Sb_2O_5 should readily form glasses but liquid Bi_2O_5 should not form a glass on ordinary cooling in air, since the estimate of ρ_1 for this oxide is $\sim 1.0-1.1$.

The changes in the configurational entropy along the M_2O_5 series were calculated using the equation (11). The entropy initially decreases with the increase in B_{12} and then goes through a shallow minimum at $B_{12} \approx 2500$ eV (see Fig. 7a). This minimum is due to the fact that the distribution of CN for the M–O pairs is rather narrow and almost symmetrical with its centre close to 5.0 for $B_{12} = 2500$ eV. When $B_{12} < 2500$ eV, the structure of oxide becomes more complex, since $z(M-O) = 4$ and 5 are almost equally probable. At $B_{12} > 3500$ eV, the CN distribution width rapidly increases, resulting in the increase in entropy. When $B_{12} \geq 5000$ eV, the width of CN distribution and the configurational entropy remain almost unchanged.

6. Models of non-crystalline oxides in the MO_3 series

Oxides of the MO_3 series include such components of glasses and metallurgic slags as CrO_3 , MoO_3 , and WO_3 . Pure MoO_3 and WO_3 form glasses on ordinary cooling of melt,¹⁴³ as well as on flattening.¹³¹ There are very few diffraction data on the structure of the MO_3 oxides. Thus, the structural information on complex oxides should be used. The study on the structure of Na_2O-WO_3 glass¹²⁶ was already cited.

A series of computer models for MO_3 oxides at 0 and 2000 K was constructed using the MD and CSR methods.¹³⁰ All models contained 500 ions in the cube. The potentials (1) with the following parameters were applied: $Z_1 = +6$, $Z_2 = -2$, $B_{11} = 0$, $B_{22} = 1500$ eV, $R_{ij} = 29$ pm. The critical value of B_{12} for this series is 1101 eV. Therefore, the values of B_{12} were chosen in the range of 1150–9999 eV. The models were constructed in a way similar to other M_mO_n series. The Coulomb interactions were taken into account using the Ewald–Hansen method.³⁹ The edge length of the basic cube was adjusted to maintain the pressure close to zero.

A model with $B_{12} = 1150$ eV was in a special position. The pressure in the system remains positive at 2000 K and at any volume, which means that the system was in the state of a strongly compressed gas. In vacuum, this gas contains the MO_3 molecules with ionic bonding in the form of centred regular triangles. Visual analysis of a spatial model constructed on the base of results of computation with $B_{12} = 1150$ eV demonstrated that the oxide is composed of separate MO_3 groups, which represent almost planar triangles with the M^{6+} ions in their centres. The planes of the triangles are randomly oriented, however there is a tendency on a

rotation of one of the vertices towards the centre of the neighbouring triangle. This arrangement gives a gain in energy. Many large pores and cavities were found in the model. The MO_3 groups are aggregated into clusters of 4–5 groups, and the clusters are relatively remote from each other.

The dependencies of the characteristics for the MO_3 models on B_{12} are shown in Fig. 8. The $r_1(ij)$ values increase monotonically with increase in B_{12} , the molar volume goes through a minimum at $B_{12} \approx 3400$ eV. As in the case of other oxides, this minimum is due to a rapid increase in CN for the M–O pairs from 3.00 at $B_{12} = 1150$ eV to ~ 6 at $B_{12} = 3400$ eV and further up to ~ 8.0 .

At $B_{12} = 3400$ eV, the M–O distance is 179 pm, which almost coincides with the W–O distance in tungstenate glasses. So far, this model can be attributed to WO_3 oxide. In fact, in addition to $r_1(M-O)$, the mean CN for the M–O pairs (6.0) also coincides with the experimental data.¹²⁶ However, the distribution of $z(M-O)$ reveals that CN equal to 5 and 7 are also present in the models, though the value 6 (octahedral arrangement) dominates.

$z(M-O)$	4	5	6	7	8	9	10
Number of M^{6+} ions with $B_{12} =$							
1850	41	66	17	—	—	—	—
3000	—	27	93	5	—	—	—
4800	—	13	97	15	—	—	—
9999	—	—	5	31	59	26	4

When $3000 \leq B_{12} \leq 4800$ eV, the majority of O^{2-} ions have two neighbouring M ions and they play a role of bridging particles linking two neighbouring MO_n groups. Only at $B_{12} = 9999$ eV, do the majority of O^{2-} ions have three M neighbours. As regards the $z(ij)$ distribution, the oxide structure with $B_{12} = 4800$ eV is the most ordered.

Distributions of CN for the O–O pairs have specific features. When $B_{12} \geq 3400$, they have an usual form with a maximum near $z(M-O) = 8-9$. However, when $B_{12} \leq 1850$ eV, these distributions exhibit two maxima at $z = 3-4$ and $6-7$. The first maximum is especially high for the model with $B_{12} = 1150$; it is attributed to the above-mentioned configuration, in which a vertex of one of the MO_3 triangles is directed towards the centre of another triangle. The first maximum is assigned to O^{2-} ions that do not link the two triangles. The second maximum is assigned to the bridging O^{2-} ions. An increase in B_{12} results in a gradual smearing of the structural elements and the system turns into the dense one. This can be seen from the values of the topological parameters ρ_1 and s . At $B_{12} = 1850$ eV, $\rho_1 = 0.780$ and $s = 2.0$; increase in B_{12} is accompanied by an increase in ρ_1 to 1.05 and a decrease in s to ~ 1.0 , which indicates the appearance of a dense structure. When $B_{12} \leq 4800$ eV, all models have loose structures.

Distributions of the O–M–O azimuthal angles are very broad (the standard deviations up to $25-30^\circ$) for all models besides the model with $B_{12} = 1150$ eV. Distributions of M–O–M angles are more narrow, their standard deviations increase from 9.2 (at $B_{12} = 1850$ eV) to 24.8° (at $B_{12} = 9999$ eV).

Taking account of ionic radii, the models were identified as follows:¹³⁰

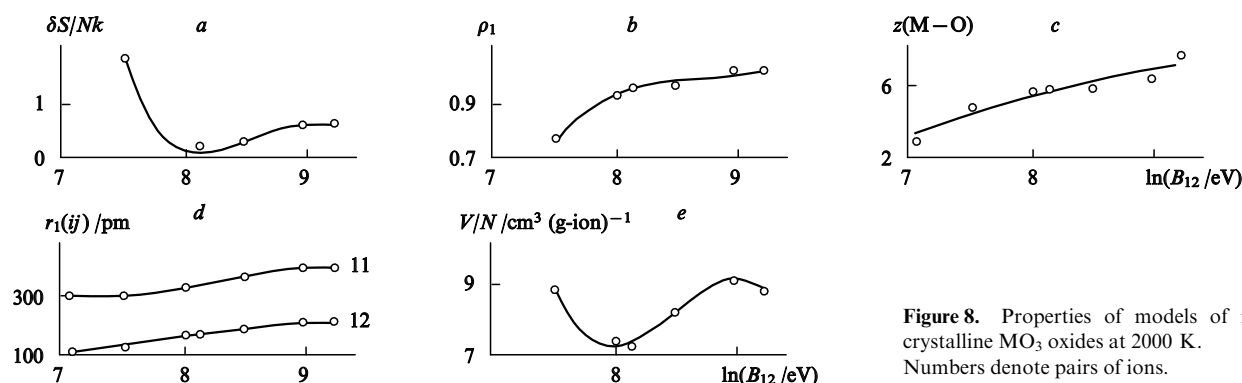


Figure 8. Properties of models of non-crystalline MO_3 oxides at 2000 K. Numbers denote pairs of ions.

MO ₃	CrO ₃	ReO ₃	TeO ₃	MoO ₃	WO ₃
B_{12} /eV	2300	2800	2930	3260	3400

Therefore, real MO₃ oxides form a rather narrow group corresponding to a small region $2300 \leq B_{12} \leq 3400$ eV in the homologous series. Other models are hypothetical.

For models of the MO₃ oxides, thermal energy at 2000 K is 0.5% of the total energy. Thus, temperature has little effect on their structure. The average heat capacity C_p is close to the classical value $3R = 24.9$ J (g-ion K)⁻¹.

Change in the configurational entropy δS along the series¹³⁰ (see Fig. 8a) has a rather deep minimum at $B_{12} \simeq 3000$ eV, and is almost constant at higher B_{12} . Again, the entropy behaviour may be explained by structural effects, although in the interval corresponding to the real oxides the entropy changes insignificantly.

VI. Simulation of binary non-crystalline oxide systems

1. Simulation of non-crystalline silicate systems

a. Models of systems of M₂O—SiO₂ type

Numerous studies are devoted to silicate systems due to their practical importance. Structural data for silicates¹⁴¹ and M₂O·2SiO₂ bisilicates¹³² were reviewed. Lithium bisilicate does not form a glass on ordinary cooling of a melt, for sodium bisilicate the glass formation is difficult, and potassium bisilicate readily forms a glass.¹⁴³ However, it was stated¹⁴⁸ that a lithium bisilicate glass was prepared by ordinary cooling of a melt. Negative deviations from the ideal thermodynamic state of M₂O were observed in M₂O—SiO₂ systems.

Experimental data on the structure of alkali metal silicates were obtained by X-ray and neutron scattering. It was established that the Si—O distance almost does not depend on the composition and temperature of oxide and is close to 161 pm, and $z(\text{Si—O}) \simeq 4.0$. For the M—O pairs (M = Li, Na, K), the M—O distance and the mean CN increases in the series Li → K. Data given by different authors disagree. For Li, the M—O distances lie in the range of 190–260 pm, for Na in the range of 222–248 pm, and for K in the range of 265–275 pm. The CN for the Li—O pairs varies from 3 to 4, for the Na—O pairs, from 4 to 6, and for K—O and Cs—O pairs, from 5 to 7.5.

It should be noted that the structural data for lithium silicates are unreliable. The contribution of the Li—O pairs to the total PCF is very small both for X-rays and neutrons, and thus this peak is almost indistinguishable in the TPCF above the background of false oscillations due to the Fourier transformation of the structural factor.

Structural studies of Na₂O—SiO₂ glasses with 19 mol.%–35 mol.% of Na₂O showed that the Na—O, Si—O, Si—Si, and O—O distances are 235, 162, 320, and 264 pm, respectively; $z(\text{Si—O}) = 4.0$ and $z(\text{Na—O}) \simeq 6$.^{149,150} For potassium silicates with 14 mol.%–20 mol.% of K₂O, the CN for the K—O pairs was $\sim 10 \pm 1$.¹⁵⁰ It was established that Na⁺ and K⁺ ions occupy pores formed by the silicon-oxygen network.

Structures of M₂O·2SiO₂ bisilicates (M = Li, Na, K), and of (Li_{0.63}Na_{0.37})₂·2SiO₂ were investigated using scattering of a pulsing neutron beam.¹⁵¹ Contributions of the Li—O pairs appeared insignificant. An approximate interpretation gave the following values of the interionic distances:

Pair	Li—O	Na—O	Si—O	O—O
$r_1(ij)$ /pm	~ 200	~ 240	161–163	263–265
$z(ij)$	—	—	3.9–4.0	4.4 (Li), 4.9 (Na)

Data on computer simulations of binary systems such as Li₂O—SiO₂,^{152–155} Na₂O—SiO₂,^{35,83,134,153,154,156–161} K₂O—SiO₂,^{153,154,161,162} as well as oxides in the M₂O·2SiO₂ series (see Ref. 132) have been published. Different potentials were applied in the simulations. In many studies,^{131,134,152,153,155,162} the potentials (1) with accurate account of the Coulomb interactions using the Ewald–Hansen method³⁹ were used. An accelerated computational scheme was developed¹⁵³ in which the Ewald sums

were calculated for the sublattice of one basic cube octant on initial steps and the interpolation was performed for all intermediate points. In¹⁵⁴ the Ewald sums were truncated. A combination of the Keating's three-particle potential for three-atom combinations of silicon and oxygen particles, with the Lennard–Jones potentials for interactions of sodium particles with the other particles was applied³⁵ for the Na₂O—SiO₂ oxides. In the majority of simulation studies, only structural aspects were carefully explored, and little attention was paid to the thermodynamic properties.

Models for M₂O—SiO₂ systems (M = Li, Na, K) comprising 800 ions in the basic cube were constructed.¹⁵⁴ Concentration of M₂O varied from 1.47 mol.% to 23 mol.%. Generally, reasonable agreement between simulation and diffraction data for melt structures was achieved.¹⁵¹ However, the Si—O distance appeared to be somewhat shorter (157 pm instead of 161–162 pm). No clustering of M⁺ ions was observed. The addition of an M₂O oxide does not affect the basic structure of silica and leads only to the appearance of non-bridging O²⁻ ions (*i.e.* particles with CN for the O—Si pairs differing from 2). The mean Si—O—Si angle was somewhat larger than the actual value ($\sim 155^\circ$ instead of $\sim 143^\circ$). This deviation can be explained by the contribution of covalent bonding to the interparticle interactions in real oxides that has not been taken into account in the model.¹⁵⁴ It was found that a change in the molar volume affects substantially the azimuthal angles and CN for the M—O pairs. Vibrational frequencies for various ions were also estimated.¹⁵⁴

Structural differences of sodium and potassium silicate glasses are due to the different degrees of nanoscale inhomogeneities in the distribution of terminal oxygen ions (which have only one silicon neighbour) and the alkali metal ions bound to them. These inhomogeneities were considered¹⁶¹ to be a specific feature of alkali-silicate glasses.

Models of a melt (1000–4000 K) and glass (300 K) of 2Li₂O·SiO₂ were constructed using the MD method and with accounting for Coulomb interactions using the Ewald method.^{152,155} The density for the model of glass was taken to be equal to the actual value. The models comprised 576 ions; the Born–Meyer potentials were used. Charges of lithium, silicon, and oxygen ions were +1, +4, and –2, respectively. Values of 160 and 186–193 pm were obtained for Si—O and Li—O distances; the mean CN for these pairs were 4.0 and 3.5, respectively. The calculated interionic distances were compared with the experimental results¹⁵¹ (see below).

Pair	Li—O	Li—Li	O—O	Li—Si	Si—Si
$r_1(ij)$ /pm					
calculation	186–193	248–260	258	306–310	320
experiment ¹⁵¹	223(?)	—	263–265	—	320

The agreement between these data is moderate, although the experimental estimates for the Li—O pairs are hardly accurate. Monomeric and dimeric structural groups SiO₄⁴⁻ (43 groups) and Si₂O₆⁶⁻ (18 groups) were found along with SiO₃²⁻ chains. The mean CN for the Li—O pairs in the models lie in the range of 3–4 (the experimental value is 3.1, see Ref. 151).

The following values of self-diffusion coefficients (D) were calculated from the slope of the regression line for ion shifts vs. time:

Ion	Li ⁺	Si ⁴⁺	O ²⁻
$10^5 D$ /cm ² s ⁻¹			
melt (3000 K)	21.5	1.88	2.23
glass (1000 K)	1.09	0.184	0.283

As could be expected, the diffusion of lithium ions is rather fast, while for silicon and oxygen the values of self-diffusion coefficients are close to the limits of the MD calculations.

Having revealed in the models the O²⁻ ions with 2 (bridging), 1 (terminal), and 0 (free) closest Si neighbours, the authors calculated the equilibrium constant for the reaction $2\text{O}^- = \text{O}^0 + \text{O}^{2-}$ in terms of the polymer theory of slags.¹⁵⁵

The constant for the $2\text{Li}_2\text{O} \cdot \text{SiO}_2$ glass at 300 K was 0.0032, which implies that almost all the oxygen atoms belong to the SiO_4^{4-} monomers.

Models of melts (2000 K) and glasses (605 K) with composition of $2\text{M}_2\text{O} \cdot \text{SiO}_2$ ($\text{M} = \text{Li}, \text{Na}, \text{K}$) were also constructed.¹⁵³ According to a more recent publication,¹⁶³ these models contained 110–120 ions in the cube. For the Li–O pairs, the distance of 260 pm was obtained. This value is definitely overestimated, since the sum of the ionic radii is $74 + 120 = 194$ pm. Self-diffusion coefficients of ions at 1010 K were also calculated in this study. The following values were obtained:

Ion	Li^+	Na^+	K^+	Si^{4+}	O^{2-}
$10^5 D / \text{cm}^2 \text{ s}^{-1}$	15	3.3	2.3	0.98	2.0

The MD method was used¹⁵⁶ to construct a model of $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$. The repulsion of ions was described by the Pauling formula (6) with the power coefficient $n = 10$. The basic cube contained 3000 ions. Interionic distances and CN were as follows:

Pair	Na–Na	Na–Si	Si–Si	Na–O	Si–O	O–O
$r_1(ij) / \text{pm}$	~310	335	312	228	162	262
$z(ij)$	–	5.1	?	5	4	–

These results are in agreement with diffraction data¹⁵¹ for the Si–O and O–O pairs.

Models of sodium silicates containing 4.846 mol.% to 30.1 mol.% of Na_2O were constructed;¹⁵⁷ the models comprised 700–900 ions. The size of the basic cube was chosen taking into account the actual density of a melt. The pair potentials (1) with parameters adjusted to the properties of α -quartz were used. The relaxation was performed in the sequence 6000–3000–1500–293 K for 10 000 steps at each temperature. The results obtained agreed well with the diffraction data. A difference in bond lengths between the silicon atom and the bridging (165 pm) and terminal (< 156 pm) oxygen atoms was observed. It was found that the portion of bridging oxygen ions with $z(\text{O}–\text{Si}) = 2$ decreases from 95% to 65% with increase in the Na_2O content, while the portion of terminal ions increases from 5% to 35%. The models were inhomogeneous on a nanometer scale, so that the sodium atoms were clustered around non-bridging oxygen atoms.

Models of amorphous (0 K) and liquid (2000 K) bisilicates $\text{M}_2\text{O} \cdot 2\text{SiO}_2$ with the Born–Meyer potentials were constructed using the CSR and MD methods.¹³² The following values of B_{ij} were selected: 0 for the M–M and M–Si pairs, 2055.4 (Si–Si), 1729.5 (Si–O), 1500 eV (O–O), and 545.3, 925.1, 1601.94, 3844.1, and 9999.0 eV for the M–O pairs in five different models. The third and the fourth models related to sodium and potassium bisilicates, respectively. The distance in the M–O pairs depends almost linearly on $\ln B_{13}$ (atom numbering is as follows: 1 for M, 2 for Si, and 3 for O). As B_{13} increases, the M–Si and M–O distances increase monotonically, the M–M distance changes non-monotonically, and the Si–Si, Si–O and O–O distances remain almost unchanged. At $B_{13} = 626.7$ eV in the model that corresponds to lithium silicate, $r_1(\text{M}–\text{O}) = 181$ pm. Diffraction data give the higher value (186–193 pm). For sodium and potassium silicates, the agreement between the corresponding values is substantially better. All model distances for sodium silicate obtained in^{132, 156} agree well with the experimental data.

The adequacy of the models constructed may be examined by comparing the calculated and actual molar volumes at 2000 K and zero pressure.

Oxide	$\text{Li}_2\text{O} \cdot 2\text{SiO}_2$	$\text{Na}_2\text{O} \cdot 2\text{SiO}_2$	$\text{K}_2\text{O} \cdot 2\text{SiO}_2$
$V/N / \text{cm}^3 (\text{g-ion})^{-1}$			
calculation	9.73	10.2	11.6
experiment ¹³³	8.1	9.5	11.6

For lithium bisilicate, the difference between the results of simulation and experimental data reaches 20%, but for sodium and potassium bisilicates it does not exceed 4%–6%. For rubidium bisilicate, the interpolation of V/N at $B_{13} = 5320$ eV

gives the value $11.9 \text{ cm}^3 (\text{g-ion})^{-1}$, while the experimental value (extrapolated to 2000 K) is 12.0 .¹³³

The reason for the deviations observed is probably the more distinct manifestation of hysteresis phenomena on going from Na to Li. At a pressure of 4 GPa and 673 K, the density of lithium silicates increases by 6%–9% in 15 min, while that of sodium trisilicate, by 3.2%, and of potassium trisilicate, by 0.2%.¹¹⁸ Overestimated molar volume for models of lithium bisilicate may be due to their metastability. Furthermore, it is also possible that the Born–Meyer potentials are poorly applicable for the description of lithium oxide.

It is noteworthy that model M–O distances^{132, 152, 155} are shorter than those obtained from diffraction studies, while the molar volume for the models is larger than that of the real oxides. This contradiction might be explained assuming that the diffraction data for the Li–O pairs are inaccurate and the PPCF peak for the Li–O pair in the total PCF is attributed incorrectly.

For MD simulation of lithium silicates, the values $B_{13} = 1443$ eV and $R_{13} = 29$ pm were selected.¹⁵⁴ The calculated M–O distance (200 pm) was close to that obtained from diffraction data. However, with this value of B_{13} the molar volume of a model Li_2O crystal was equal to the actual value [$4.974 \text{ cm}^3 (\text{g-ion})^{-1}$] only at a pressure of 98 GPa. Thus, the assumption on overestimated Li–O distances obtained from diffraction studies seems reasonable.

The CN values for the M–O pairs in the models of bisilicates¹³² were as follows:

B_{12} / eV	545.3	925.1	1601.9	3844.1	9999.0
$z(\text{M}–\text{O})$					
2000 K	2.48	3.36	4.97	5.41	6.10
0 K	2.20	2.54	3.59	5.21	7.15

In M_2O crystals, the CN for the M–O pairs is 4.0. Melting or amorphisation are accompanied by a decrease in the CN. On going from a simple oxide to bisilicate, the CN increases substantially and when $B_{13} \geq 1601$ eV it already exceeds 4. For sodium bisilicates, the agreement between $z(\text{M}–\text{O})$ obtained from the simulation (4.97 at 2000 K) and diffraction (5.8 at 1373 K, see Refs 51, 141) is quite reasonable.

An increase in CN for the M–O pairs on going from simple oxide to bisilicate at $B_{13} \geq 1601$ eV is partially due to an abrupt decrease in the molar volume, although the formation of a silicate network is another important factor. In the case of M^{n+} ions with $n \geq 2$ (for example, Ca^{2+}), the transition from MO to $\text{MO} \cdot 2\text{SiO}_2$ leads to a relatively small change in the CN for the M–O pairs (from 5.1 in CaO to 5.6 in bisilicate). This can be explained by the fact that ions with charges ≥ 2 form a coordination sphere around O^{2-} ions, and its structure is almost independent of the composition of the complex oxide.

Interparticle distances for the O–O pairs may be compared with those obtained from the diffraction analysis. In real lithium, sodium, and potassium silicates, $r_1(\text{O}–\text{O}) = 263$ –266 pm.^{141, 151} This distance in the models is 259–262 pm.^{132, 156} Small deviations are probably due to the use of different computational schemes. The experimental values for $z(\text{O}–\text{O})$ appeared equal to 5.6 for all bisilicates,¹⁴¹ while the model CN gradually decrease from 5.75 at $B_{13} = 545.3$ eV to 4.89 at $B_{13} = 9999$ eV.¹³² The agreement of these results may be regarded as good, since the PPCF peaks of the Na–O and K–O pairs overlap with the peaks of the O–O pairs, which makes accurate calculations of partial CN difficult. In this sense, the simulation gives more precise results.

Analysis of the shape of TPCF for bisilicates at 2000 K (for X-rays) obtained from simulations demonstrated that peaks assigned to the Li–Li, Li–Si, and Li–O pairs are totally absent due to the small scattering factor of lithium atom. For potassium silicate, K–O and Si–O peaks do not overlap. Comparison of these data with the diffraction data¹⁴¹ showed that the assignment of peaks¹⁴¹ is in accordance with the results of simulation only in the case of potassium bisilicate. When $r > 500$ pm, the TPCF are

virtually equal to the asymptotic value of 1.00 due to a mutual interference of oscillations of six PPCF.

Comparison of the experimental data with the results of simulations shows that in diffraction studies of multi-component systems a correct interpretation can be made, in the best case, only for one or two first TPCF peaks. Consequently, the computer simulation of these systems is of special importance.

Additional information on the structure of compounds considered may be extracted from the $z(\text{O}-\text{O})$ distributions in bisilicates. The distributions exhibit two maxima at CN equal to 3 and 6. For instance, the CN distribution for binary $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ oxide has the form:¹³²

$z(\text{O}-\text{O})$	2	3	4	5	6	7	8	9	10
Number of Na^+ ions	—	64	23	9	118	48	11	1	—

The value 3 is typical of isolated SiO_4^{4-} tetrahedra and CN 6 is typical of two linked tetrahedra with a shared vertex. In the model of SiO_2 at 2000 K, $z(\text{O}-\text{O})$ lies in the range from 5 to 12 with a strong maximum at 6–7, and the mean CN is 7.14. Therefore the presence of values $z < 5$ in bisilicates indicates partial decomposition of an oxygen-silicon network and the appearance of unshared vertices. Oxygen ions occupying these vertices, according to the polymer theory of slags, are called terminal O^- ions. If the radii of the closest spheres for the $\text{O}-\text{O}$ and $\text{O}-\text{Si}$ pairs were identical, the number of terminal O^- ions would be equal to the number of O^{2-} ions with $z(\text{O}-\text{Si}) = 1$.

For the $\text{M}-\text{O}$ pairs, the distributions of CN are very broad (for instance, in sodium bisilicate the CN values lie in the range from 2 to 8, and for potassium bisilicate, in the range from 3 to 11). Hence, ions with charge +1 cannot form a rigid coordination sphere around them. Small ions with large charge, such as Si^{4+} , can do this: 100 out of 110 Si^{4+} ions have exactly four O^{2-} neighbours. Spatial distribution of neighbours around Si^{4+} ions is approximately tetrahedral, the $\text{O}-\text{Si}-\text{O}$ azimuthal angles are $109^\circ \pm (11-13^\circ)$. The mean value of the $\text{O}-\text{Si}-\text{O}$ angle is close to the ideal tetrahedral value, but this distribution is rather broad. The values of $\text{M}-\text{O}-\text{M}$ angles vary from Li to Cs over a wide range, although their mean value is almost constant ($93-97^\circ$).

The topological characteristics of the above models are as follows:

B_{13} / eV	545.3	925.1	1601.9	3844.1	9999.0
ρ_1	0.886	0.930	0.959	0.962	0.988
s	2.05	1.77	1.42	1.60	1.42

It is seen that the structure of alkali metal bisilicates is loose, and when $B_{13} \leq 925$ eV the values of ρ_1 are even lower than for pure silica (0.93). The addition of M_2O oxide with small M^+ ions (such as Li^+) results in the increase in the looseness of the system and in the appearance of large cavities (pores) therein.

The thermodynamic properties of liquid and amorphous bisilicates were simulated.¹³² It was established that the increase in B_{13} leads to a gradual increase in the molar volume. The ratio of molar volumes $V_{2000\text{ K}}/V_{0\text{ K}}$ is close to 1.00 at $B_{13} = 545.3$ eV and increases to 1.12 for $B_{13} = 9999$ eV. The mean heat capacity C_p of the oxides is close to $3R$. Changes in volume in the formation of one mole of a complex oxide from the simple ones is positive for $B_{13} \leq 1602$ eV and negative for $B_{13} \geq 3844$ eV. The change in energy in the formation of one mole of bisilicate is negative for all values of B_{13} and lies in the range from -27 kJ mol $^{-1}$ to -118 kJ mol $^{-1}$. Therefore, negative deviations from the ideality should be observed for these oxides. The values of ΔE_{form} found are very close to the experimental heats of formation of the corresponding crystalline lithium, sodium, and potassium bisilicates. Thus, the ionic model of complex oxides works adequately in respect of their thermodynamic properties. Even selection of a very simple form of the pair potentials (1) leads to agreement with the experimental data.

Changes in the Gibbs energy and entropy along the $\text{M}_2\text{O} \cdot 2\text{SiO}_2$ series were calculated according to the equation (11).¹³² It was established that the increase in B_{13} is accompanied

by a decrease in ΔG_{form} (formation of a complex oxide from the simple ones). These results are not only in qualitative, but (for lithium and sodium bisilicates) also in quantitative agreement with the experimental data. Values of ΔG_{form} for other silicates were predicted.¹³² It was shown that the configurational entropy passes through a minimum at $B_{13} = 1602$ eV as B_{13} increases and then increases by only $\sim 0.4Nk$. Changes in entropy ΔS in a formation of one mole of a complex oxide from the simple ones depends on B_{13} in a similar way and has a minimum at $B_{13} = 3844$ eV.

Models of oxides in a binary $(\text{Na}_2\text{O})_x(\text{SiO}_2)_{1-x}$ system composed of 500 ions with various x were constructed using the CSR and MD methods with the pair potentials (1).¹³⁴ The results of the simulation are summarised in Table 5.

The values of molar volumes were obtained with an error of several percent due to slow changes in pressure in the CSR calculations. Therefore, the molar volume changes non-monotonically as a function of composition. Nevertheless, there is a distinct minimum of the molar volume at $x = 0.2-0.3$. In general, a noticeable compression of a system occurs in the formation of binary oxides from pure non-crystalline Na_2O and SiO_2 (by 8%–9% in middle range of compositions). Comparison with the experimental data for the crystalline compounds demonstrated that the calculated volume of glass exceeds the corresponding experimental value by $\sim 10\%$ in all cases. The energy of glasses per one mole of a complex oxide depends virtually linearly on x with deviations from additivity not exceeding 1.2%. Changes in the energy ΔE_{form} are positive for $x < 0.5$ and negative for $x > 0.5$. In the case of potassium silicate at 1200 K, the transition of excess enthalpy ΔH_{form} to positive values is almost unnoticeable.¹⁶² The error in the determination of ΔE_{form} is 15 to 20 kJ (g-ion) $^{-1}$. The experimental values for the partial enthalpy of SiO_2 at $x = 0.10-0.22$ and $T = 1200-1800$ K is ~ 0.9 kJ mol $^{-1}$, i.e. substantially less than the error of simulation.

Positions of PPCF peaks obtained in simulation are in good agreement with the experimental data (see above), especially for sodium bisilicate. The TPCF calculated for this model agrees well with the published data¹⁶⁵ but differs from those from another study.¹⁶⁴ Positions of the peaks found in Ref.¹³⁴ are in agreement with the results of calculation.¹⁵⁶ Longer Na–Na, Na–O and shorter Na–Si distances were obtained in a simulation with the use of three-particle potentials.³⁵

Distributions of CN for the Na–O pairs appeared rather broad; for instance, at $x = 0.666$, the values of $z(\text{Na}-\text{O})$ lie in the range from 1 to 7 and the mean CN is 3.33 ± 0.95 . Distribution of $\text{O}-\text{Si}-\text{O}$ angles lies within the range of $90-140^\circ$ ($114 \pm 8.4^\circ$). Therefore, the distribution of O^{2-} ions around Si^{4+} ions is mostly tetrahedral, though 9% of silicon ions have two, three, or five O^{2-} neighbours.

Neglecting an Ewald potential terms with a cubic symmetry (in order to save computational time) may lead to serious errors. For example, at $x = 0.5$ the Na–Na distance without taking account of the cubic contributions is 258 pm, while accounting for these terms gives 288 pm; Na–Si distances are 261 and 313 pm,

Table 5. Parameters of models of glasses in the system $(\text{Na}_2\text{O})_x(\text{SiO}_2)_{1-x}$ at 0 K.

Parameter	x	1.0	0.8	0.67	0.5	0.33	0.2	0.1	0.0
V/N / cm ^{3} mol $^{-1}$		27.6	28.4	25.3	27.3	25.8	25.4	26.5	27.2
$r_1(ij)$ / pm for pairs									
Na–O		222	229	229	228	233	226	237	—
Si–O (exp. ¹⁶⁴)		—	160	160	161	163	162	161	161
Na–O		—	—	—	235	236	—	—	—
Si–O		—	—	—	162	162	—	—	—
ρ_1		1.073	1.01	1.03	0.98	1.00	0.96	0.93	0.93

respectively. Thus, the simplification of the computational algorithm is not always justified.

When $T = 0$ K and $x \leq 0.5$, the energy of formation $\Delta E_{\text{form}} > 0$, so that a tendency for separation of components should be observed. This point was specially considered for a $\text{K}_2\text{O}-\text{SiO}_2$ system.¹⁶² It was shown that K^+ ions occupy large pores of the oxygen-silicon network. Basing on analysis of diffraction data, it was proposed¹⁶⁵ that the melt (glass) is built up of two types of microgroups, viz. with high alkali metal content ($\text{Na}_2\text{O} \cdot 2\text{SiO}_2$) and with high silicon content (with composition close to silica) in the range $0.2 \leq x \leq 0.33$. These microgroups cannot exist in models with $N \approx 500$.

The addition of Na_2O to SiO_2 leads to a rapid increase in ρ_1 and abrupt decrease in s . Therefore, the addition of Na_2O causes an effective depolymerisation of the structure, i.e. a decomposition of the tetrahedral network of bonds. The system is depolymerised to a noticeable degree already at $x = 0.5$. Models³⁵ constructed with accounting of three-particle potentials give higher values of ρ_1 . For example, a calculation³⁵ at $x = 0.333$ gave the value of $\rho_1 = 1.056$, which is typical of dense non-crystalline systems. Results of simulation^{134, 156} agree well with each other in respect of ρ_1 (for instance, at $x = 0.33$, $\rho_1 \approx 0.96$).

The applicability of the polymer theory of slags (PTS) to the $\text{Na}_2\text{O}-\text{SiO}_2$ oxides was analysed.¹³⁴ The basic parameters of this theory are the degree of polymerisation α , molar ratios of different anions, and polymerisation constant K_p . Solutions of associates are usually regarded as ideal ones. To use a polymer model, the following conditions have to be met: 1) CN for the Si-O pairs has to be equal to 4 for all Si atoms; 2) the oxygen atom with two closest silicon neighbours is considered as a 'bridging' O^0 atom; 3) the oxygen atom with one closest silicon neighbour is considered as a 'terminal' O^- atom; 4) 'free' oxygen O^{2-} ion does not have any closest Si neighbours.

Further, the n_0 , n_1 , and n_2 will be used to denote numbers of 'bridging', 'terminal' atoms, and 'free' ions, respectively. The degree of polymerisation is given by the formula:¹³⁴

$$\alpha = n_0 [2n(\text{Si})]^{-1},$$

where $n(\text{Si})$ is a number of silicon ions. For pure SiO_2 , $\alpha = 1$ if all O particles have two Si neighbours. The polymerisation constant is defined as the equilibrium constant for the reaction $2\text{O}^- = \text{O}^0 + \text{O}^{2-}$ within the ideal solution approximation.

$$K_p = X(\text{O}^0)X(\text{O}^{2-}) [X(\text{O}^-)]^{-2},$$

where $X(\text{O}_k) = n_k/n(\text{O})$ is a ratio of O_k particles to the total number of oxygen particles in the system. The α and K_p parameters can be calculated from the computer simulations. For models of $(\text{Na}_2\text{O})_x(\text{SiO}_2)_{1-x}$ glasses, the following values were found:

x	0.800	0.667	0.500	0.333	0.20
α	0.197	0.336	0.542	0.715	0.87
K_p	0.104	0.064	0.027	0.044	0.051

K_p were determined approximately due to the small value of n_2 for $x \leq 0.5$. If the condition $z(\text{Si}-\text{O}) = 4.00$ (for each silicon ion), as well as the condition on the electrical neutrality of the system are met, the following expression holds:¹³⁴

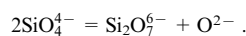
$$K_p = \frac{\alpha[x - 2(1-x)(1-\alpha)]}{8(1-x)(1-\alpha)^2}.$$

This expression holds satisfactorily for sodium silicate models.

In order to determine the polyanionic composition of a model in terms of the PTS, it is necessary to distinguish complex $\text{Si}_m\text{O}_n^{q-}$ anions as bound groups of particles in which each silicon atom is linked to at least one other silicon atom of the same group through a bridging oxygen atom. Distributions of the bound groups calculated for $(\text{Na}_2\text{O})_x(\text{SiO}_2)_{1-x}$ models are shown below:

x	0.8	0.667	0.5	0.333
Group	$1^{12}2^64^{15}1$	$1^{11}2^43^24^{17}1^{19}1$	$1^32^31^68^1$	110^1

The notation $1^{12}2^6\dots$ means that 12 SiO_4^{4-} 'monomers', 6 $\text{Si}_2\text{O}_7^{6-}$ dimers, and so on, were found in the model. When $x \leq 0.333$, all oxides are completely polymerised (in accordance with the PTS). Another PTS parameter is the equilibrium K_{11} constant for the reaction



Within the ideal solution approximation K_{11} is given by:

$$K_{11} = n_2 n(\text{Si}_2\text{O}_7^{6-}) [n(\text{SiO}_4^{4-})]^{-2}.$$

Values of K_{11} for models of sodium silicate vary in a wide range (from 1.56 at $x = 0.5$ to 3.46 at $x = 0.8$).

In agreement with the PTS, ionic ratios $Y(i)$ are defined as ratios of numbers of polyanions composed of i particles to the total number of all polyanions and free anions O^{2-} ; the ionic ratio $Y(\text{O}^{2-})$ is defined similarly. These parameters characterising the anionic composition of silicates only slightly depend on temperature.

In terms of the theory of perfect ionic solutions, the thermodynamic activity of M_2O in $\text{M}_2\text{O}-\text{SiO}_2$ oxides is equal to the ionic ratio $Y(\text{O}^{2-})$. It was found¹³⁴ that in an $(\text{Na}_2\text{O})_x(\text{SiO}_2)_{1-x}$ system $Y(\text{O}^{2-})$ is always close to x , i.e. the solutions should be ideal. In fact, however, strong negative deviations from the ideal state are observed for Na_2O ; and the activity coefficient of Na_2O at $x = 0.6$ and $T = 2000$ K is 0.092. Nevertheless, the value of $Y(\text{O}^{2-})$ under these conditions is ~ 0.60 .

Therefore, the polymer theory of slags, being self-consistent to some extent (in respect of concentrations of different types of particles and polyanions), does not predict correctly the thermodynamic activity of the components. Therefore, the PTS parameters (α , K_p) obtained from a fit to the thermodynamic properties rather than to the structural data, are only effective measures. Within this approximation, the PTS is simplified (like the model of associated solutions).

Models of $\text{Na}_2\text{Si}_2\text{O}_5$ glass were constructed using the MD method in a temperature range of 1000–2000 K (1080 ions, density of 2.5656 g cm^{-3}).¹⁵⁹ The potentials proposed earlier¹⁶⁶ included pairwise and three-particle interactions. The Coulomb terms were calculated according to Ewald. It was shown that PCF and structural factor of the model at 1000 K are in good agreement with the diffraction data and with the results of MD simulation of sodium silicate¹⁵⁷ with the Buckingham potentials.¹⁶⁷ It was found that 98% of silicon ions have CN of 4.0% and 2% have CN of 3.0. Only 5% of oxygen ions are bridging and therefore do not have neighbouring sodium ions. Sodium ions are situated in pores of the silicate network close to the terminal oxygen atoms and diffuse between site positions of the structure via a jumping mechanism. The value of activation energy of self-diffusion of sodium ions (54.3 kJ mol^{-1}) was close to the experimental value (66.6 kJ mol^{-1}).

The penetration of inert gases (Ne, Ar, N_2) into SiO_2 , Na_2SiO_3 , $\text{Na}_2\text{Si}_2\text{O}_5$, and sodium-aluminosilicate glasses was investigated using the MD method.¹⁶⁸ The results of the simulation demonstrated that none of the above glasses absorbs nitrogen and argon, while neon can penetrate into the first three of them.

b. Models of $\text{MO}-\text{SiO}_2$ systems

The structure of liquid FeO was investigated by X-ray anomalous scattering.^{141, 169} In the simulation of the oxide, B_{ij} values for Fe–O and O–O pairs were adjusted to achieve the agreement between the simulated interionic distances and the experimental results.¹⁷⁰ The following values were obtained: $B_{11} = 1300$, $B_{12} = 1900$, $B_{22} = 1500 \text{ eV}$ (alternatively, the value of $B_{22} = 905.6$ was taken⁹). The agreement between the results of simulation and the diffraction data was good (Table 6). Using the same B_{ij} values and taking $R_{ij} = 29 \text{ pm}$, reasonably good agreement with the experimental data was achieved for energy, molar volume, and compressibility of FeO crystals.

Table 6. Interionic distances and coordination numbers for liquid FeO.

Parameter	Model for FeO (see Ref. 170)	Experiment ¹⁶⁹
r_1 /pm for pairs		
Fe–Fe	313	315
Fe–O	207	205
O–O	317	320
z for pairs		
Fe–Fe	12.6	11.8
Fe–O	5.8	5.7
O–O	12.3	12.2

The structure of some non-crystalline oxide systems, *viz.*, FeO–SiO₂, MgO–SiO₂, and CaO–SiO₂ were investigated by X-ray scattering.^{51, 141, 171} Interionic distances were determined by interpretation of certain TPCF peaks. Structural analysis of MgSiO₃¹⁷² and CaSiO₃¹⁷³ glasses was performed. Structure of CaSiO₃ glass was also studied by X-ray diffraction and Raman spectroscopy. The TPCF exhibits only three peaks at 164 pm, 243 pm, and 364 pm. The Raman spectrum for this glass was similar to the corresponding spectra of pyroxenes, which contain chains of SiO₄^{4–} tetrahedra linked through vertices as the main structural elements; the chains are linked to each other *via* Ca²⁺ ions. Ring anions, such as Si₄O₁₂^{8–}, Si₅O₁₅^{10–}, were rare. The peak at 164 pm was attributed to the Si–O pairs. The maximum at 243 pm was a result of overlapping of Ca–O and O–O contributions. A structural model of CaSiO₃ glass based on the pyroxene structure was proposed,¹⁷³ in this model one half of oxygen atoms were bridging.

In the case of an MgSiO₃ glass, the X-ray TPCF contains five peaks.¹⁷² A peak at 163 pm was attributed to the Si–O pairs, and at 208 pm to the Mg–O pairs (the sum of the ionic radii of Mg and O is 207 pm). The mean CN for the Mg–O pairs was 4.1. A structural model of an MgSiO₃ glass was also constructed on the basis of the pyroxene structure. There, the main structural elements were also chains of SiO₄^{4–} tetrahedra linked through vertices. The magnesium ions are situated between the chains. Each Mg²⁺ ion has four oxygen neighbours at a distance of 208 pm and two more neighbours at a distance of 250 pm. Mg²⁺ ions occupy two types of sites: in almost ideal octahedral sites with $z = 6$ and in rather irregular sites with $z = 7$.

The Born–Meyer pair potentials were used in simulations of 2MO·SiO₂ (M = Mg, Ca, Sr, Ba, Fe),^{136–139} CaO–SiO₂ (see Ref. 65), and FeO–SiO₂ (see Ref. 170) complex oxides. The following values for parameters were taken (numbering of atoms: 1 states for M, 2 for Si, 3 for O): $B_{11} = B_{12} = 0$, $B_{22} = 2055.4$ eV,⁹ $B_{23} = 1729.5$,⁹ $B_{33} = 1500$, and $R_{ij} = 29$ pm. Models of (FeO)_{*x*}(SiO₂)_{1–*x*} for the whole range of compositions $0 \leq x \leq 1$ were constructed.¹⁷⁰ The models contained ~ 500 ions in the basic cube. Densities were taken from a reference book.¹⁷⁴ The Coulomb interactions were taken into account using the Ewald–Hansen method.³⁹ Positive deviations from the ideal state found for the energy of formation amounted to few tens kJ mol^{–1}. The experimental values of changes in energy in the formation of a complex oxide lie in the range from –6.3 kJ mol^{–1} to 2.5 kJ mol^{–1}. The heat of formation for crystalline fayalite (2FeO·SiO₂) is 33.5 kJ mol^{–1}. The Fe–O and Si–O distances depend insignificantly on the composition of the binary oxides.¹⁷⁰ For other pairs, this dependence is more pronounced though also not very strong. The results of the simulation showed that the interpretation of diffraction data is not correct for complex oxides in all cases due to a possibility of attributing false TPCF peaks to the real ones.

Distributions of CN for the Fe–O pairs in (FeO)_{*x*}(SiO₂)_{1–*x*} models are rather broad. For instance, at $x = 0.5$ and $T = 2000$ K, $2 \leq z(\text{Fe–O}) \leq 5$ (the mean value is 3.3); in the fayalite ($x = 2/3$), $2 \leq z(\text{Fe–O}) \leq 6$ and the percentage of Fe²⁺

ions in octahedral coordination is 2.1%. Measurements of the Mossbauer effect in silicate slags gave close estimates (1.1%–2.0%).¹⁷⁵ Most of Fe²⁺ ions in the models have three or four O^{2–} neighbours.

Distributions of O–Fe–O, Fe–O–Fe, O–Si–O, and Si–O–Si azimuthal angles for linked three-atom combinations were calculated.¹⁷⁰ Distributions of Fe–O–Fe and O–Fe–O angles are spread over the range of 45–180° and have a flat maximum near 90°. The diffusion corresponds to scatter of the CN values for the Fe–O and O–Fe pairs. For the O–Si–O angles, the coordination sphere radius was adjusted to obtain $z(\text{Si–O}) = 4$. In this case, the distribution of the $\theta(\text{O–Si–O})$ angles is a Gaussian with $\theta = 108 \pm 15^\circ$. The width of this distribution is equal to the corresponding width obtained for the model of SiO₂ at 2500 K.⁵⁵ Hence, on going from pure silica to fayalite the configuration of ions in SiO₄^{4–} groups changes insignificantly. However, the models considered¹⁷⁰ are closer to the tetrahedral configuration than other models.⁵⁵ The distribution of angles in fayalite generally agree with the diffraction data.¹⁷⁶

The topological parameter ρ_1 for pure FeO is 1.08, *i.e.* the structure of the oxide is dense. The addition of SiO₂ is accompanied by increase in the structural looseness. The following parameters were found for a model of FeO at 2000 K:¹⁷⁰

x	1.00	0.80	0.67	0.50	0.25	0
ρ_1	1.08	0.98	1.00	0.96	0.93	0.93
s	1.13	0.90	1.08	1.19	1.40	1.62

It is clearly seen that the addition of FeO to SiO₂ initially affects ρ_1 insignificantly, and for $x \leq 0.4$ the depolymerisation of the tetrahedral network does not take place. However, in the range $0.5 \leq x \leq 0.6$ the ρ_1 parameter increases due to the transition to a dense structure with the octahedral coordination. In fact, at $x = 0.5$ the CN $z(\text{Fe–O}) = 3.5$ and at $x = 0.667$, $z(\text{Fe–O}) = 4.0$, while for pure FeO $z(\text{Fe–O}) = 5.8$. The short-range order in FeO is analogous to that in liquid NaCl.

The adequacy of the PTS for (FeO)_{*x*}(SiO₂)_{1–*x*} was examined.¹⁷⁰ The main condition of the theory, $z(\text{Si–O}) = 4$, is not met for all silicon atoms, but the number of Si ions with three or five O^{2–} neighbours is relatively small.

$z(\text{Si–O})$	3	4	5
$x = 0.8$	5	35	5
0.667	7	58	6
0.5	5	89	6
0.25	15	105	15
0	4	75	3

The values of α and K_p were calculated from n_0 , n_1 , and n_2 (the numbers of oxygen ions), and the distributions of Si_{*m*}O_{*n*} bound groups were also found (Table 7).¹⁷⁰

The bound group distribution shows that for $x \leq 0.5$, the system is almost completely polymerised. Cyclic anions were absent in the models.

'Polymerisation constants' K_p listed in Table 7 depend on the FeO content: they increase with increase in x (as in the Na₂O–SiO₂ system). This increase does not agree with the model of ideal polymer solution. Values of K_p obtained in different studies were summarised.¹⁷⁷ The value 0.08 obtained in Ref. 178 at 1573 K is

Table 7. Characteristics of models of (FeO)_{*x*}(SiO₂)_{1–*x*} oxides.

x	α	K_p	K_{11}	Bound groups	$X(\text{O}^{2-})$
0.8	0.19	0.085	3.3	1 ¹⁶² 8 ³ 3 ⁴ 1	0.79
0.667	0.34	0.072	0.68	1 ¹⁵² 3 ³² 6 ¹⁹ 12 ¹ 17 ¹	0.68
0.5	0.56	0.039	—	1 ¹⁴ 19 ⁵ 1	(0.78)
0.25	0.82	(0.025)	—	135 ¹	(0.5)

Note. Values with low precision are indicated in parentheses.

the closest to data of Ref. 170, but the majority of K_p values calculated by fitting to the thermodynamic activities of components lies in the range of 0.7–2.0. As in the case of sodium silicates, these polymerisation constants are effective parameters and they do not describe the real structure. The K_{11} values also strongly depend on the composition.

The results of simulation of $(\text{FeO})_x(\text{SiO}_2)_{1-x}$ oxides showed that for $x \leq 0.5$ the system is almost completely polymerised to form a spatial silicon-oxygen network.¹⁷⁰ A loose structure with the low mean CN is maintained there. An assumption on predominance of linear and cyclic anions¹⁷⁹ in the range $0.2 \leq x \leq 0.5$ was not confirmed. The relatively slight dependence of K_p on concentration is in agreement with the associated ideal solution theory. In the thermodynamic respect, the $\text{FeO}-\text{SiO}_2$ system is close to the ideal one. The calculated activity of FeO for $x \geq 0.667$ is in reasonable agreement with the experimental data. Therefore, the PTS model reflects correctly some substantial features of structures of $\text{FeO}-\text{SiO}_2$ melts and glasses for $x \geq 0.5$. However, for lower x values the model is inadequate due to virtually complete polymerisation of the system.

The proportions of oxygen particles present as 'free' O^{2-} ions or included into SiO_4^{4-} groups calculated by different authors for the $\text{FeO}-\text{SiO}_2$ melts were summarised.¹⁸⁰ Results of computer simulation are in good agreement with the computation.¹⁸¹ For other systems (for example, sodium silicates), such agreement was not achieved.

It should be taken into consideration that the interpretation¹⁷⁰ of the polymerisation is purely structural, since it does not assume the formation of the valence bonds, and it is due to sum of the Coulomb forces and forces of the electron shell repulsion. Therefore, the reason for the polymerisation in ionic models is totally different from that underlying the PTS. The agreement of the results of simulation with the conclusions from PTS for $x > 0.5$ is probably due to the fact that the adequacy of the PTS is defined directly by the structure rather than by bonding type that determines the structure.

A similar study of structures and the properties of $(\text{CaO})_x(\text{SiO}_2)_{1-x}$ oxides at 2000 K was performed.⁶⁵ The metasilicate ($x = 0.5$) is formed from simple liquid oxides with a decrease in volume by $\sim 5\%$. Changes in the energy in the formation of the metasilicate is $-4.8 \pm 20 \text{ kJ mol}^{-1}$; the experimental value is -40 kJ mol^{-1} . The reasonable agreement between the simulated characteristics and the experimental results^{51,141} as regards the positions of the TPCF peaks and CN was achieved. The majority of Ca^{2+} ions have five or six oxygen neighbours, however $\text{Ca}-\text{O}$ pairs with CN ranging from 3 to 9 are also present.

The addition of CaO to SiO_2 leads to a linear increase in ρ_1 up to 1.00 at $x = 0.5$. But the addition of FeO initially almost does not change ρ_1 . The smaller Fe^{2+} ion deforms the network structure not as strongly as the Ca^{2+} ion. However, already when $x \geq 0.65$ the difference between the structures of these silicates becomes insignificant.

The PTS was also applied to analyse the structures of $\text{CaO}-\text{SiO}_2$ models.⁶⁵ The difference between $\text{FeO}-\text{SiO}_2$ and

$\text{CaO}-\text{SiO}_2$ systems in terms of degree of polymerisation α , polymerisation constant K_p , and the bound group distribution, is rather small. When $x \leq 0.5$, the polymerisation is almost complete. However, the deviations from the ideal state for the $\text{CaO}-\text{SiO}_2$ system are negative and significant. Adjustment of the activity coefficients within different version of the PTS gives the value of $K_p \approx 0.0016-0.0045$.¹⁷⁷ The difference between these (effective) K_p and the value found by the structural analysis is due to the inadequacy of the ideal PTS modification and probably due to an insufficient model size.

A series of models of $2\text{MO} \cdot \text{SiO}_2$ oxides was constructed using the Born–Meyer potentials ($B_{13} = 1441.4-8885.1 \text{ eV}$).¹³⁷⁻¹³⁹ Additionally, two hypothetical models with $B_{13} = 500 \text{ eV}$ and 800 eV were also considered.¹³⁶ Each model contained 497 ions. Figure 9 illustrates some properties of the models. The molar volume depends on non-monotonically B_{13} . It has a minimum near 800–1000 eV. The molar volume of simple MO oxides similarly depends on B_{13} . An increase in the volume at $B_{13} < 800 \text{ eV}$ indicates an abrupt increase in the structural looseness of the oxide. The interparticle $r_1(\text{M}-\text{O})$ distances for the models increases gradually with an increase in B_{13} . The transition from pure MO to the silicate affects the $r_1(\text{M}-\text{O})$ distance insignificantly. A similar effect was observed for CN of the $\text{M}-\text{O}$ pairs. At $B_{13} = 500 \text{ eV}$, the value of $z(\text{M}-\text{O})$ in the orthosilicate is 2.00, which indicates the presence of chain structural elements. At $B_{13} = 800 \text{ eV}$, $z(\text{M}-\text{O}) = 3.3$, *i.e.* the trigonal elements should dominate in the structure. For simple MO oxides, the CN for the $\text{M}-\text{O}$ pairs with the same values of B_{13} are 2.0 and 3.5, respectively (see above). Hence, the structure of first coordination spheres of M^{2+} ions are the same in both the orthosilicate and the simple oxide. The addition of SiO_2 leads to a broadening of the $\text{O}-\text{M}-\text{O}$ angle distributions, *i.e.* results in a certain disordering of the oxide structure.

It should be noted that the $\text{Mg}-\text{O}$ distance behaves abnormally for magnesium orthosilicate.¹³⁹ This distance for the model at 2000 K (196 pm) is substantially shorter than the experimental value (208–216 pm). Coordination numbers for the $\text{M}-\text{O}$ pairs are also noticeably smaller (3.7 instead of 4.7–5.0). The repulsion parameter for the $\text{Mg}-\text{O}$ pairs was determined from the compressibility data for MgO crystals. Presumably, this characteristic has to be corrected for a non-crystalline phase.

A specific arrangement of the $\text{O}-\text{O}$ pairs with maxima of distributions of their CN at $z = 3$ and 6 was found for models with $B_{13} = 3283-8885$ (from calcium to barium silicate). A reason for the appearance of these maxima becomes obvious on consideration of the spatial models.¹³⁶ Silicon ions are situated in almost planar parallel layers separated by $\sim 0.61 \text{ nm}$. A layer of SiO_4^{4-} corresponds to each Si^{4+} layer. The centre of the model is occupied by a figure composed of two SiO_4 tetrahedra linked through a shared vertex to form an almost ideal trigonal prism Si_2O_7 the centre and six vertices of which are occupied by the O^{2-} ions. The central O^{2-} ions have CN for the $\text{O}-\text{O}$ pairs equal to 6, and each O^{2-} ion in the vertices of the prism has three O neighbours. The

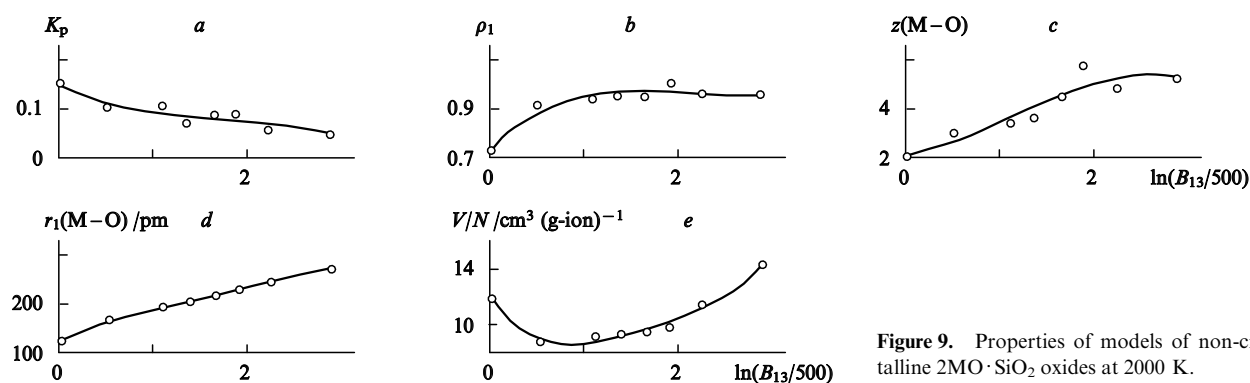


Figure 9. Properties of models of non-crystalline $2\text{MO} \cdot \text{SiO}_2$ oxides at 2000 K.

ratio of the ions with CN 3 and 6 is 6. In models of $\text{MO} \cdot \text{SiO}_2$ oxides, the similar type of ordering of O^{2-} ions was revealed.

Thus, for $2\text{MO} \cdot \text{SiO}_2$ oxides with large M^{2+} ions (such as Ba^{2+}) an association of silicate tetrahedra to form Si_2O_7 trigonal prisms with approximately layered arrangement of tetrahedra is typical. The space between layers is loosely filled with M ions and some of the O ions. A part of M ions is situated in the layers as well. Large pores with an average radius of ~ 0.44 nm (the size of ions was not taken into account) were also observed. A decrease in the size of M ions leads to their stronger interactions with oxygen ions. As a result, M ions begin to form bridges between the SiO_4^{4-} tetrahedra and between the tetrahedra and oxygen ions as well. This leads to a disordering of the structure and to its loosening. It is clearly seen from the plots of ρ_1 and s vs. B_{13} (see Fig. 9). An analysis of bound group distribution demonstrated that the increase in B_{13} is accompanied by the increase in the number of monomers and a decrease in the size of bound groups.

A series of MD models for an $(\text{MnO})_x(\text{SiO}_2)_{1-x}$ system was constructed¹⁶² using the potentials (1). The heat of formation for the models was negative for $x > 0.4$ and positive for the models high silica content. This corresponds to a stratification of a liquid phase in the system. The reason for the switching of the ΔH_{form} sign lies in the strong effect of small Mn^{2+} ions on the structure of the silicon-oxygen network. The smaller M^{2+} ions, the stronger the distortion of the network and the higher the energy of the system, leads to a broadening of the area of stratification of a liquid phase in the binary $\text{MO}-\text{SiO}_2$ system.¹⁶²

The applicability of the PTS to orthosilicates at various B_{13} was examined.¹³⁶ An increase in B_{13} from 500 to 8885 eV leads to a decrease in K_p by a factor of 3 (see Fig. 9). The effective values of K_p calculated according to the thermodynamic activity of MO oxide vary over a substantially wider range: from 1.0 in iron silicates to 3×10^{-4} in barium silicates.¹⁸² The difference from the structural data is due to the non-ideal nature of the solutions.

Calculation of the changes in configurational entropy along the $2\text{MO} \cdot \text{SiO}_2$ series showed that the transition to values $B_{13} < 1441.4$ eV leads to a decrease in the entropy.¹³⁶ When B_{13} grows in the range 1441–1900 eV, the entropy passes through a flat maximum and further remains almost constant. The entropy of simple MO oxides behaves similarly (see Fig. 4).

Changes in the Gibbs energy in the formation of orthosilicates starting from simple oxides are positive for $B_{13} \leq 1441$ eV. This indicates the instability of the complex oxide with respect to probable decomposition into two phases. In fact, in $\text{BeO}-\text{SiO}_2$ and $\text{MgO}-\text{SiO}_2$ systems at 2000 K the area of a monophase liquid is very narrow. However, in the $\text{FeO}-\text{SiO}_2$ system ($B_{13} = 1900$ eV) this area becomes much broader.

A model of amorphous $\text{ZnO} \cdot 3\text{SiO}_2$ using the MD method with the BMH potentials was constructed.¹⁸³ The model contained 264 ions, viz. Zn^{2+} , Si^{4+} , and O^{2-} , in the basic cube with the edge of 15.38 pm (the density is 2.87 g cm^{-3}). First, heating of the system up to 10 000 K followed by cooling to 300 K in ~ 30 ps were simulated. As a result, the first PPCF peaks appeared isolated, the Si–O, Si–Si, and Zn–O distances were 162 pm, 318 pm, and 198 pm, respectively. The mean CN for the Zn–O pairs was estimated (not very reliably) as 4.41, since coordination numbers 4 and 5 were predominant in the distribution in accordance with the diffraction data. For Zn^{2+} ions with CN of 4.0, the mean Zn–O distance was 197 pm and 204 pm for ions with CN 6. According to the shape of the PPCF for the O–O pairs, a conclusion was made on the presence in the structures of SiO_4 tetrahedra linked *via* edges. In this case, the CN of the corresponding Si ions is 5; this results in a low value of the O–Si–O angle (89°). The majority of oxygen ions adjacent to Zn ions have three neighbours. In general, the arrangement of particles in the model resembled that in ZnSiO_3 crystal of the pyroxene type. MD data demonstrated that Zn cannot completely substitute silicon atoms in the network and therefore destroys the silicon framework.

c. Models of $\text{M}_2\text{O}_3-\text{SiO}_2$ systems

$(\text{B}_2\text{O}_3)_x(\text{SiO}_2)_{1-x}$ melts readily form glasses, while the $(\text{Al}_2\text{O}_3)_x(\text{SiO}_2)_{1-x}$ oxides form glasses only for $x < 0.65$. Among the systems considered, only the structure of the $(\text{Al}_2\text{O}_3)_x(\text{SiO}_2)_{1-x}$ glasses (see Ref. 184) was studied experimentally. It was established that for $x = 0.061-0.469$ the position of the first TPCF peaks shifts monotonically from 162 to 179 pm with increase in x . Since this peak is a result of overlapping of Si–O and M–O contributions and the $r_1(\text{Si}-\text{O})$ distance is 161–162 pm, the M–O distance may be estimated as 199 pm. The O–O distance is 260 pm.

It is usually assumed that the amorphous Al_2O_3 oxide may act both as a modifier and a network-forming component, *i.e.* aluminium particles can either occupy cavities between the SiO_4^{4-} tetrahedra or substitute the silicon atoms in the silicon-oxygen network. The CN for the Al–O pairs are usually 4 or 6.

The following oxide systems were studied by the computer simulation methods: $\text{B}_2\text{O}_3-\text{SiO}_2$,⁶⁴ $\text{Al}_2\text{O}_3-\text{SiO}_2$,⁶⁶ $\text{Fe}_2\text{O}_3-\text{SiO}_2$,¹⁰⁴ and the $\text{M}_2\text{O}_3 \cdot \text{SiO}_2$ series (see Refs 185, 186). The potentials (1) were used in these studies, the potential parameters were taken from the corresponding models of pure M_2O_3 oxides. The Coulomb interactions were taken into account using the Ewald–Hansen method.³⁹ Each model contained ~ 500 ions in the basic cube.

It was demonstrated that the molar volume of $(\text{B}_2\text{O}_3)_x(\text{SiO}_2)_{1-x}$ oxides decreases substantially in the formation of a complex oxide from the simple non-crystalline ones (by 12% for $x = 0.667$). The energy of the complex oxide formation appeared very small for $x \geq 0.7$, for the lower x and $T = 0$ K it is positive and reaches the value 42 kJ mol^{-1} ; however, this energy is negative at 2000 K. Hence, cooling of the system results in destabilisation of the oxide thermodynamically.

First TPCF peaks are split into two narrow subpeaks that represent contributions of the B–O and Si–O pairs. The height of the left subpeak (at 134–139 pm) increases and the height of the right one (at 161–162 pm) decreases as x decreases. Most of B ions have three oxygen neighbours and Si ions have four oxygen neighbours. Spatial arrangement of neighbours around the boron and silicon ions are almost independent of each other. The structure of all oxides is loose, the ρ_1 parameter increases from 0.79–0.83 in B_2O_3 to 0.93 in SiO_2 (with a small minimum at $x = 0.5$). It was concluded⁶⁴ that the $\text{B}_2\text{O}_3-\text{SiO}_2$ oxide are copolymers of two B_2O_3 and SiO_2 polymers. The BO_3^{3-} and SiO_4^{4-} are linked through shared vertices as a result of random combination of the two figures.

Models of the $\text{Al}_2\text{O}_3-\text{SiO}_2$ oxides at 0 K and 2000 K were constructed using the MD and CSR methods.⁶⁶ Each model contained ~ 500 ions. The potentials (1) were used. The increase in the molar volume in the formation of a complex oxide from the simple ones at 0 K was 10% for $x = 0.5$, and ΔE_{form} was $70-100 \text{ kJ mol}^{-1}$ for $x = 0.2-0.667$. Therefore, the system exhibits positive deviations from the ideal state. The addition of small amounts of Al_2O_3 to SiO_2 results in an abrupt increase in energy, and therefore the amorphous phase appears thermodynamically unstable at 0 K. The positive ΔV_{form} remains at $T = 2000$ K, but ΔE_{form} changes the sign, which means that liquid oxides are formed from the simple oxides with the liberation of heat. The experimental values of ΔE_{form} are very small (of the order of several kJ mol^{-1}).

The Al ions with $z(\text{Al}-\text{O}) = 4$ dominate in the models. The portion of these ions increases from 51% for $x = 1.0$ to 76% for $x = 0.2$. These values are in agreement with the estimates based on viscosity of the melts. A decrease in x favours the transition of Al^{3+} ions into the coordination state with the CN 4 and their inclusion into the tetrahedral network. Therefore, for $x < 0.4$ the value of ρ_1 is almost constant. The coordination number 6 is rather rare ($< 6\%$). After 4, the most typical value of CN is 5. It was shown⁶⁶ that the PTS can be applied to the $\text{Al}_2\text{O}_3-\text{SiO}_2$ oxides if the inclusion of the ions into the tetrahedral network is

taken into consideration. The K_p constant varies from 0.21 ($x = 1$) to 0.15 ($x = 0.2$).

2. Simulation of borate systems

The results of simulation of $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ ionic glasses using the MD method have been published.⁸⁴ An addition of sodium oxide leads to the increase in CN for the B–O pairs from 3 to 4, and sodium atoms occupy the nearest pores of the structure. The changes in the CN of boron atoms was confirmed by the NMR data.¹⁸⁷

The structure of $\text{B}_2\text{O}_3-\text{Li}_2\text{O}$ glasses with 0%, 10%, and 20% of Li_2O were studied¹⁸⁸ using the X-ray scattering and MD-simulation. The potentials (1) were applied. The models contained from 1656 to 1728 ions in the basic cube. It appeared that the B–B and Li–O distances did not depend on the concentration, and the structure is built of the randomly linked BO_3 and BO_4 groups. The lithium ions are weakly bound with the boron ions and are located mostly in pores of the boron-oxygen network. The vibrational spectra of the glasses were also calculated. They resembled the IR-absorption spectra, but differ from the Raman spectra.

Models of B_2O_3 and $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ were constructed using the MD method with the mixed ion-covalent potentials.¹⁸⁹ The Born–Meyer potentials (1) were applied for all pairs of atoms; additionally, the three-particle potentials were used for O–B–O and O–B–B combinations. For the $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ oxide the value of 3.4 for $z(\text{B}-\text{O})$ was obtained, which is in agreement with the results for lithium borate.¹⁸⁸

Nanoscale structural inhomogeneities for the alkali-borate glasses both in liquid and glassy states were revealed by the small angle X-ray scattering.⁸² In order to reproduce this effect in MD-models, the size of the models has to be enlarged substantially.

Simulation of the crystallisation process of liquid $2\text{MgO} \cdot \text{B}_2\text{O}_3$ using the MC method was performed.¹⁹⁰

3. Simulation of phosphate and vanadate glasses

Structures of the metaphosphate glasses containing Zn, Mg, Ca, Sr, Ba, and Na were studied by X-ray diffraction methods.¹⁹¹ The following values of CN for the M–O pairs were found:

M	Zn	Mg	Ca	Sr	Ba	Na
$z(\text{M}-\text{O})$	4.1	4.6	6.8	7.0	7.8	5.7

For Ca, Sr, Ba, and Na the CN are close to those in crystalline compounds, but the values for Zn and Mg are abnormal.

Models of $(\text{CaO})_x(\text{P}_2\text{O}_5)_{1-x}$ oxides with $x = 0.8, 0.667, 0.5, 0.333$, and 0.2 were constructed¹¹⁷ using the Born–Meyer potentials with the charge of phosphorus atoms equal to +5. The Coulomb interactions were taken into account using the Ewald–Hansen method.³⁹ Such characteristics of the metaphosphates, as $r_1(\text{P}-\text{O}) = 155$ pm and the molar volume of $8.40 \text{ cm}^3 (\text{g-ion})^{-1}$ were reproduced with high accuracy. The values of ΔE_{form} reached -66 kJ mol^{-1} , which is extremely small compared to the total molar energies of the oxides (from -3405 for CaO to $-36\,930 \text{ kJ mol}^{-1}$ for P_2O_5 at 2000 K). However, these values are significant if compared with the $RT = 16.6 \text{ kJ mol}^{-1}$. Thus, the negative deviations from the ideal state should be expected. Changes in the volume of the system in the formation of one mole of a complex oxide are always positive and equal to $5.26 \text{ cm}^3 \text{ mol}^{-1}$ for the metaphosphate at 2000 K.

The calculated TPCF for X-rays has only three distinct maxima. The first one is attributed to the P–O pairs, the second one is a result of overlapping of Ca–O and O–O contributions. The third maximum is a result of overlapping of Ca–Ca, Ca–P, and P–O contributions. Therefore a reliable interpretation of the experimental diffraction data for these complex oxides is very difficult. The $r_1(\text{P}-\text{O})$ distance depends slightly on the CaO concentration (it changes from 150 pm for $x = 0.80$ to 159 pm for $x = 0$). For the metaphosphate, $r_1(\text{P}-\text{O}) = 153-156$ pm. For the phosphorus ions with $z(\text{P}-\text{O}) = 5$, the distance is slightly longer than for the ions with $z(\text{P}-\text{O}) = 4$.

The distributions of CN for the P–O pairs are given below:

$z(\text{P}-\text{O})$	$x = 0.8$	0.667	0.5	0.333	$x = 0.0$
4	33	40	30	18	19
5	31	46	71	94	105
6	2	4	9	12	18

The tetrahedral coordination of the phosphorus ions dominates (50%) for $x = 0.8$; with a decrease in x , the maximum of the distribution shifts to $x = 5$. In pure P_2O_5 , the CN varies in the range 4–6: ca. 13%–14% of P^{5+} ions in the oxide have $z(\text{P}-\text{O}) = 4$ or 6. The less the P_2O_5 concentration in the model, the greater the portion of the phosphorus ions having $z(\text{P}-\text{O}) = 4$. Diffraction data usually give the values of CN for the P–O pairs close to 4 and even less (to 3.8).¹⁹² Therefore, the Born–Meyer potentials with charge of the phosphorus ions equal to +5 do not allow one to obtain purely tetrahedral coordination of the phosphorus ions in the models. Presumably, this fact is indicative of the substantial contribution of the covalent bonding in phosphates.

For the Ca–O pairs, the following values of CN were found: 5.6 in pure CaO , 4.7 for the model with $x = 0.5$; for $x = 0.333$, the CN increases up to 6.5.¹¹⁷ The diffraction data¹⁹³ reveal a minimum of the CN values at $x = 0.333$; usually, the CN values given by the diffraction exceed the simulation data by ~ 1.5 . This difference is due to different schemes used for calculation of the CN.

The distributions of CN for the O–O pairs have specific features. For pure P_2O_5 , the distribution has a usual form, i.e. a curve with a broad maximum at CN $z = 7$. The same shape is maintained at $x = 0.333$, but an additional maximum appears at the CN of 4. In the range $0.500 < x < 0.800$, the distributions of $z(\text{O}-\text{O})$ exhibit two maxima: $z(\text{O}-\text{O}) = 3$ and 6–7. A similar effect was observed earlier for the computer models of complex oxides, such as $2\text{MO} \cdot \text{SiO}_2$ and $\text{M}_2\text{O} \cdot 2\text{SiO}_2$ (see above). This is due to the formation of rather rigid coordination spheres composed of O^{2-} ions surrounding the central metal ions (like SiO_4^{4-}) and fusion of these groups through a shared vertex. If $z(\text{P}-\text{O}) = 4$, then in such a distorted tetrahedron each O^{2-} ion has three O^{2-} neighbours, i.e. $z(\text{O}-\text{O}) = 3$. In the case of $z(\text{P}-\text{O}) = 5$, the coordination sphere of the P^{5+} ion is a trigonal bipyramid and two out of five O^{2-} ions have $z(\text{O}-\text{O}) = 3$ and three O^{2-} ions have $z(\text{O}-\text{O}) = 4$. In the fusion of two groups with $z(\text{P}-\text{O}) = 4$, the common O^{2-} ion has $z(\text{O}-\text{O}) = 6$. For the fusion of two groups with $z(\text{P}-\text{O}) = 4$ and 5 or 5 and 5, the common O^{2-} ion may have $z(\text{O}-\text{O})$ from 6 to 8.

At $x = 0$, the model almost does not contain O^{2-} ions with $z(\text{O}-\text{O}) = 3$. Hence, each O^{2-} ion has two P^{5+} neighbours and is shared between two PO_5 groups. It is clearly seen from the distributions of CN for the P–O pairs. For $x = 0.333$, ca. 20% of O^{2-} ions have $z(\text{O}-\text{P}) = 1$ and for these ions $z(\text{O}-\text{O}) = 3-4$. However, O^{2-} ions with $z(\text{O}-\text{P}) = 2$ should have $z(\text{O}-\text{O}) = 6-7$. Therefore, the distribution of $z(\text{O}-\text{O})$ exhibits two maxima, viz., a small peak at CN $z = 4$ and a high one at CN $z = 7$. When $x \geq 0.500$, the two maxima are maintained in the $z(\text{O}-\text{O})$ distribution but the height of the peak at $z(\text{O}-\text{O}) = 6$ decreases with growth of x due to decrease in the number of O^{2-} ions which have two P^{5+} neighbours.

The distributions of the O–P–O azimuthal angles are very broad for all compositions and do not indicate the presence of any specific configurations of ions. This is caused by the rather broad distributions of $z(\text{P}-\text{O})$. With a decrease in x , the proportion of large bound groups increases, and at $x \leq 0.500$ the complete polymerisation of the structure occurs.

A probable contribution of a ring component to the structure was also analysed. Rings with a minimum size more than eight members were totally absent. A decrease in x results in an increase in the number of rings, and the six- and eight-membered rings predominate in the structure. The four-membered rings are almost absent due to the high energy of the corresponding spatial figure.

For all values of $x < 0.8$, the structure of oxides appeared loose. According to the ρ_1 values (from 0.96 for $x = 0.8$ to 0.93 for $x = 0$), the $\text{CaO}-\text{P}_2\text{O}_5$ oxides should readily form glasses when $x < 0.8$. But in practice for the $\text{CaO}-\text{P}_2\text{O}_5$ system it is possible to obtain glass by rapid cooling only at $x < 0.57$.¹¹⁸ The difference between these limits is noticeable; it indicates that several additional effects leading to the crystallisation of real calcium phosphates with high CaO content, exist.

A model of AlPO_4 glass (192 particles in the basic cube) was built by MD method with the Born–Meyer potentials.¹⁹⁴ A total time for one run was 24 ps (2 ps at 20 000 K, 2 ps at 10 000 K, and 20 ps at 1500 K). It was established that the structure is a network of AlO_4 and PO_4 tetrahedra fused to each other through vertices like in silica. However, a proportion of oxygen ions are terminal. The calculated TPCF are in reasonable agreement with the experimental data.¹⁹⁵

Pair	P–O	Al–O	O–O	P–P	Al–P	Al–Al
$r_1(ij)$ /pm						
calculation	150	180	245	320	325	330
experiment ¹⁹⁵	160	160	260	310	310	310

The distributions of CN are as follows: $z(\text{P}-\text{O}) = 4$ (96.7%) and 5 (3.3%), $z(\text{Al}-\text{O}) = 3$ (10%) and 4 (90%). The mean $\text{P}-\text{O}-\text{P}$ angle is 164° . The network of bonds in the model is not perfect, but it is generally more ordered than in silica. It is possible that the structure of aluminium phosphate contains clusters linked by bridging oxygen ions.

Models of $2\text{ZnO} \cdot \text{P}_2\text{O}_5$ and $2\text{Na}_2\text{O} \cdot \text{P}_2\text{O}_5$ glasses containing 407 and 481 ions in the basic cube were constructed.¹⁹⁶ The Born–Meyer potentials were used. The PO_4 tetrahedra were the main structural elements of the models obtained, they can aggregate to form larger polymeric groups. The degree of polymerisation and the portion of long chains are less in sodium phosphate. Fragments with branching points are totally absent. The sodium and zinc ions occupy randomly the cavities of the tetrahedral network. The coordination numbers for the $\text{Na}-\text{O}$ pairs lie in the range from 3 to 6 and from 4 to 6 for $\text{Zn}-\text{O}$.

A model of $\text{Pb}(\text{PO}_3)_2$ was also constructed¹⁹⁷ using the MD method. The force functions (6) were applied (the functions were assumed to be zero for distances $r > 0.55$ nm). The interaction parameters were adjusted so as to achieve agreement between peak positions for the calculated and experimental TPCF.

Ion	O	P	Pb
r_i /pm	120	15	99
Z_i	−1.136	2.840	1.136

The Coulomb interactions were taken into account approximately. The model contained 630 ions in the basic cube. Cooling of the system from 15000 K to 300 K was performed at an average rate of $1.23 \times 10^{13} \text{ K s}^{-1}$. The final density of the glass was taken equal to the actual value (4.74 g cm^{-3}).

It was shown that the models of crystalline metaphosphate contain chains of the PO_4 tetrahedra linked through their vertices. The chains are linked to each other via Pb^{2+} ions, which are attracted to non-bridging oxygen ions. The following distances were found in the crystal: 156 and 146 pm ($\text{P}-\text{O}$), 235 and 261 pm ($\text{O}-\text{O}$), 289 and 301 pm ($\text{P}-\text{P}$), and 382 pm ($\text{Pb}-\text{Pb}$). For models of the glass, the first PPCF peak for the $\text{P}-\text{O}$ pairs was isolated with positions of 145 pm and CN equal to 4.0. This distance is shorter than the value found in amorphous iron-lead metaphosphate (155–158 pm, see Ref. 198) and in nickel-copper pyrophosphate (154.3–154.5 pm, see Ref. 192) using the X-ray diffraction methods, but it is close to the value (150 pm) obtained in Ref. 199. The distributions of the $\text{O}-\text{P}-\text{O}$ and $\text{P}-\text{O}-\text{P}$ azimuthal angles (from 95° to 125° and from 130° to 180° , respectively) demonstrate that the orientation of the neighbouring PO_4 tetrahedra is random. No fusion of the tetrahedra via their edges or faces was found. The following values were obtained for the interatomic distances and the coordination numbers:

Pair	O–O	O–Pb	P–Pb	O–P	P–P	Pb–Pb
$r_1(ij)$ /pm	245	243	371	151	304	390
CN	5.82	6.94	5.50	4.00	2.00	5.00

Therefore, only distances for the $\text{P}-\text{P}$ and $\text{Pb}-\text{Pb}$ pairs change noticeably upon amorphisation.

An analysis of the bound groups distribution in the model revealed linear chains comprising from one to eleven PO_4 tetrahedra, rings of 5–10 tetrahedra, and larger associates.¹⁹⁷ A secondary network, which is formed by the lead ions bound to non-bridging oxygen ions, was also found.

A structural model for a $\text{Ba}(\text{PO}_3)_2$ glass with the phosphate network composed of the PO_4 tetrahedra was constructed by the MC method based on the neutron scattering and NMR data.²⁰⁰

One of the possible reasons for the non-coincidence of the results of different simulations of non-crystalline phosphates is the use of different density values. If the density is chosen to be equal to that of the real glass, the calculated pressure may appear strongly negative or positive. Since it is for the phosphate systems that the most substantial differences were observed, this indicates again the insufficient accuracy of the Born–Meyer potentials due to the neglecting of the covalent contribution.

Models of the $(\text{CaO})_x(\text{V}_2\text{O}_5)_{1-x}$ oxides were constructed using the MD method.²⁰¹ The Born–Meyer potentials (1) were applied. The value of B_{ij} for the $\text{V}-\text{O}$ pairs was selected to be 2970 eV. The charges were +2, +5, and −2 for calcium, vanadium, and oxygen ions, respectively. Changes in the energy in the formation of a complex oxide from the simple ones was negative in all cases reaching the value -43 kJ mol^{-1} for $x = 0.5$. The $\text{V}-\text{V}$ and $\text{V}-\text{O}$ distances were virtually the same (350 and 180 pm) for all the compositions. It was demonstrated that the increase in the CaO content leads to a gradual transition from a loose network structure to a dense one. At $x = 0.333$ and 0.5, the network is built up of oxygen polyhedra arranged around the vanadium ions and linked through their vertices. The coordination numbers of the vanadium ions for such compositions are close to 5.

4. Simulation of tungstate glasses

Models of $\text{Na}_2\text{O}-\text{WO}_3$ (see Ref. 127) and $\text{CaO}-\text{WO}_3$ (see Ref. 128) systems were studied by the MD and CSR methods. The Born–Meyer potentials (1) were used; the value for the $B(\text{W}-\text{O})$ parameter was chosen to be 3400 eV. The models with 100 mol.%, 80 mol.%, 60 mol.%, 40 mol.%, 20 mol.%, and 0 mol.% of WO_3 were considered. An increase in the molar volume (by 10%) was found for the $\text{Na}_2\text{O}-\text{WO}_3$ in the formation of a complex oxide from the simple ones. The value of ΔE_{form} for 60% of Na_2O at 2000 K was -102 kJ mol^{-1} . It was shown that the distributions of $z(\text{W}-\text{O})$ are rather narrow and have the centres near 6. The mean CN values depend insignificantly on the composition (varying from 5.7 to 6). However, the distribution of the $\text{O}-\text{W}-\text{O}$ azimuthal angles is rather broad ($90 \pm 10^\circ$). Hence, for the preferred octahedral coordination of the W^{6+} ions the arrangement of oxygen ions around the W^{6+} may differ substantially for different ions. In general, W^{6+} ions form their closest coordination sphere not so rigidly as Si^{4+} ions in silicates.

In pure WO_3 and in oxides with the WO_3 content more than 50%, almost all the oxygen ions have CN equal to 2, *i.e.* they are bridging particles (in terms of the PTS). The addition of Na_2O results in a decrease in the number of such ions, *i.e.* the depolymerisation of the network of the $\text{W}-\text{O}$ bonds occurs. The distribution of the $\text{W}-\text{O}-\text{W}$ azimuthal angles is very broad, and the mean values decrease from 150° to 135° with an increase in Na_2O concentration. The distributions of CN for the $\text{Na}-\text{O}$ pairs are broad, this is due to the fact that relatively large sodium ions cannot form a stable coordination sphere. In the topological sense, all the models containing WO_3 were loose with values of ρ_1 in the range from 0.98 to 0.96; the s factor varied in the range from 1.06 to 1.55.

For the molar volume of the $(\text{CaO})_x(\text{WO}_3)_{1-x}$ system positive deviations from the additivity (up to $2.35 \text{ cm}^3 \text{ mol}^{-1}$ for $x = 0.8$) were observed; for the energy, negative deviations were observed (up to -101 kJ mol^{-1} for $x = 0.6$) similar to the $\text{Na}_2\text{O}-\text{WO}_3$ system. Presumably, this type of deviation is typical of systems including cations with strongly different charges. The negative deviations for the energy could be anticipated, since stable compounds are formed in the $\text{CaO}-\text{WO}_3$ system.

Positions of the first TPCF peaks for the $\text{Ca}-\text{W}$, $\text{W}-\text{W}$, $\text{Ca}-\text{O}$, and $\text{W}-\text{O}$ pairs depend insignificantly on the concentration. For pairs of oppositely charged ions ($\text{Ca}-\text{O}$, $\text{W}-\text{O}$) it is not surprising, but for the $\text{Ca}-\text{W}$ and $\text{W}-\text{W}$ pairs such behaviour is anomalous. This may be due to strong indirect interactions of these ions via intermediate O^{2-} ions. The value of $r_1(\text{W}-\text{O}) = 177-179 \text{ pm}$ is close to the corresponding value for real $\text{Na}_2\text{O}-\text{WO}_3$ glasses ($\sim 180 \text{ pm}$) and for models of these oxides ($172-180 \text{ pm}$). In the $\text{CaO}-\text{WO}_3$ models, the $r_1(\text{W}-\text{O})$ distances depend on the WO_3 concentration weaker than in the sodium tungstenate models.

The mean CN for the $\text{Ca}-\text{O}$ pairs decrease noticeably with a decrease in x . To the contrary, for ions with a high charge, such as W^{6+} , the mean $z(\text{W}-\text{O})$ is virtually constant over the whole range of the concentrations and very close to 6. The tungsten particles form rather stable octahedral WO_6 groups with the neighbouring oxygen atoms. For the $\text{Na}_2\text{O}-\text{WO}_3$ system at 2000 K, the mean $z(\text{W}-\text{O}) = 5.52-5.93$, *i.e.* the addition of Na_2O distorts the octahedral structure more than that of CaO . In the ideal octahedron, the $r_1(\text{O}-\text{O})$ distance should be equal to $\sqrt{2}r_1(\text{W}-\text{O})$. This expression holds with good accuracy. The distribution of the $\text{O}-\text{W}-\text{O}$ azimuthal angles for the complex oxide has two maxima with the most probable values of ~ 90 and 173° . These angles are typical of a distorted octahedron with the tungsten ion in its centre and oxygen ions in the vertices.

The distributions of CN for different pairs of ions have specific features. For the $\text{W}-\text{O}$ pairs, these distributions are very narrow, especially when $x \geq 0.4$. For $x = 0.8$, only 2.5% of the W ions have five oxygen neighbours. When $x \leq 0.2$, the distribution becomes slightly broader and the percentage of the 'oddly' coordinated tungsten ions reaches $\sim 14\%$. The distributions of $z(\text{O}-\text{O})$ for $x \leq 0.4$ have two maxima, *viz.*, at CN equal to 4 and 8. The value of 4 corresponds to the oxygen ions in one of the vertices of an isolated WO_6 octahedron. The value $z = 8$ corresponds to the oxygen ions that are common for two fused octahedra. The decrease in x from 0.8 to 0 is accompanied by a gradual decrease in the portion of oxygen ions with $z(\text{W}-\text{O}) = 4$; and these ions are totally absent in pure WO_3 oxide. This is caused by the aggregation of the WO_6 octahedra into the united polymer network.

In the case of models of the $3\text{CaO} \cdot 2\text{WO}_3$ oxide at 2000 K, the first TPCF peaks for the $\text{Ca}-\text{Ca}$, $\text{Ca}-\text{W}$, $\text{Ca}-\text{O}$, and $\text{O}-\text{O}$ pairs are relatively small, while peaks for the $\text{W}-\text{W}$ and $\text{W}-\text{O}$ pairs are much higher. For the $\text{W}-\text{O}$ pairs, this behaviour is not surprising, since it is a result of strong attraction of oppositely charged tungsten and oxygen ions. However, for the $\text{W}-\text{W}$ pairs this effect had not been observed earlier. The first PPCF peak for the $\text{W}-\text{W}$ pairs is almost completely isolated, which indicates the highly ordered mutual arrangement of the tungsten ions. Since these ions repel, the reason for the ordering should be their indirect interactions via intermediate oxygen ions. If $\text{W}-\text{O}$ distance is strictly fixed and the angle formed by vectors from an oxygen atom to two closest W neighbours is close to 180° , then the $\text{W}-\text{W}$ distance should be close to $2r_1(\text{W}-\text{O})$, *i.e.* 354 pm. The actual value of $r_1(\text{W}-\text{W})$ is 358 pm. The data show that the octahedral WO_6 groups linked via a shared vertex are ordered in such a way that their spatial diagonals passing through this vertex have a tendency to be arranged along certain direction. The $\text{W}-\text{O}-\text{W}$ azimuthal angles in the models vary from 135 to 178° , and their mean value is $151.8 \pm 15.9^\circ$.

The analysis of the Voronoi polyhedra^{43,44} constructed for the central tungsten ions demonstrates that the dominant polyhedra

(from 92.5% for $x = 0.8$ to 63% for $x = 0.2$) have the form 0-6-0-0, which corresponds to the cube, that is the Voronoi polyhedron for an ideal octahedron (the notation 0-6-0-0 means the numbers of triangular, rectangular, *etc.* faces of the polyhedron). There are 59 polyhedra of the 0-6-0-0 type and 29 polyhedra of the 1-3-3-0 type (the cube with truncated vertex) in pure WO_3 . Overall, they constitute 70% of all polyhedra for the model considered. The volume of the polyhedron with a tungsten atom increases with a decrease in x , and the distribution of the volumes broadens. For instance, at $x = 0.8$ the volumes of the polyhedra are equal to $5928 \pm 231 \text{ pm}^3$, and at $x = 0$ they are $6506 \pm 458 \text{ pm}^3$. The degree of sphericity also decreases from 0.511 to 0.488. The mean face areas depend only slightly on the concentration x but the width of their distribution increases as x decreases. Therefore, the increase in the WO_3 content results in disordering of the Voronoi polyhedra constructed around the tungsten atoms.

A study of the 'polymerisation' in the $\text{CaO}-\text{WO}_3$ oxides was performed by analysis of the W_mO_n bound groups. The tungsten atoms with a common oxygen neighbour at a distance shorter than 200 pm were considered as a group. For this distance, $z(\text{W}-\text{O}) \simeq 6.0$, and in addition no $\text{O}-\text{O}$ pairs were found, *i.e.* all the oxygen atoms have only W neighbours. The following bound groups were found in the models:

x	0.8	0.6	0.4	0.2	0.0
Group	$1^5 2^3 5^5 18^1$	$1^7 12^1 51^1$	93^1	108^1	125^1

The notation $1^5 2^3 \dots$ means that five WO_6^{6-} monomers, three $\text{W}_2\text{O}_{11}^{10-}$ dimers, and so on were found in the model. When $x \leq 0.4$, the system is completely polymerised, for $x = 0.6$ and 0.8 there exist isolated monomers surrounded only by CaO matrix. The models of $\text{Na}_2\text{O}-\text{WO}_3$ oxides behave similarly.

For $x = 0.8$, only one eight-membered ring was found in the model. The distribution of the bound groups demonstrates that this ring is a part of a bound group of 18 tungsten ions. For $x = 0.6$, 21 rings were found that included about 60 tungsten ions. Since the model contained only 70 ions altogether, the most of them were included into the ring. A comparison with the bound group distribution showed that these rings are not isolated but they are incorporated into two 12^1 and 51^1 groups. Attempts to account all these sophisticated 'polyanions' would result in a substantial complication of the polymer theory.

Finally, all rings found in the models with $x \leq 0.4$ belong to one bound group containing all tungsten ions of the models, since the oxides are completely polymerised for such concentration.

5. Simulation of other binary oxide systems

Models of binary $(\text{CaO})_x(\text{Fe}_2\text{O}_3)_{1-x}$ systems and oxides of the $\text{CaO} \cdot \text{M}_2\text{O}_3$ series were constructed^{202, 203} using the MD and CSR methods. The Born-Meyer potentials (1) were applied. The change in the molar volume in the formation of a complex oxide in the $\text{CaO}-\text{Fe}_2\text{O}_3$ system at 2000 K was small, this parameter is positive for $x = 0.5-0.7$ and negative for $x = 0.333$. The value of ΔE_{form} does not exceed 45 kJ mol^{-1} . According to the values of the heats of formation, the oxides in this system are close to the ideal ones. At 0 K, the values of ΔE_{form} are positive, so the oxides should readily decompose. It was shown that Ca^{2+} and Fe^{3+} ions form their first coordination spheres virtually independent of the value of x . The mean CN for the $\text{Ca}-\text{O}$ pairs is 5.0-5.2, and $z(\text{Fe}-\text{O})$ is 4.7-5.3. The topological characteristics point to the dense structures.

Models of oxides in the $\text{CaO} \cdot \text{M}_2\text{O}_3$ series at 2000 K were constructed using the potentials (1).²⁰³ The B_{23} parameter for the $\text{M}-\text{O}$ pairs (numbering of atoms as follows: 1 for Ca, 2 for M, and 3 for O) varied in the range of 800-5000 eV. It was demonstrated that the molar volume has a minimum at $B_{23} = 1480 \text{ eV}$, which corresponds to the $\text{CaO} \cdot \text{Al}_2\text{O}_3$ system. The coordination numbers for the $\text{Ca}-\text{O}$ pairs were close to 6 in all cases, and $z(\text{M}-\text{O})$ increases gradually from 3.3 ($B_{23} = 800 \text{ eV}$) to 5.9 ($B_{23} = 5000 \text{ eV}$). For $B_{23} = 1470 \text{ eV}$, most

M^{3+} ions have four O^{2-} neighbours; a distorted octahedral packing dominates. At higher B_{23} values, the structure is dense. When B_{23} increases from 800 to 2453 eV the configurational entropy of the oxides initially increases slightly and then again decreases slightly. A decrease in the size of M^{3+} can result in an increase in the negative deviations from the ideal state (as regards thermodynamics).

Models of oxides in the $FeO-Fe_2O_3$ system with 0 mol.%, 25 mol.%, 50 mol.%, 75 mol.%, and 100 mol.% of FeO at 0 K and 2000 K were constructed using the MD and CSR methods.¹⁰⁵ Change in the molar volume in the formation of complex oxides from the simple ones was positive (up to $4.3 \text{ cm}^3 \text{ mol}^{-1}$), the value of ΔE_{form} was also positive and did not exceed 27 kJ mol^{-1} . It was established that the structure of the coordination spheres of Fe^{2+} and Fe^{3+} in glasses and melts almost was not changed with variation of the FeO content. The topological parameter ρ_1 has a minimum (1.02) at 60% of FeO , which indicates small looseness of these oxides. The results of computer simulation¹⁰⁵ allowed one to estimate the equilibrium oxygen pressure over the $FeO-Fe_2O_3$ oxides. It was possible to predict the decomposition of magnetite Fe_3O_4 on heating, but the accuracy in determination of the decomposition temperature was not very high.

Solutions of oxygen in Fe_2O_3 at 0 K and 2000 K were studied by the MD and CSR methods.¹⁰⁶ In order to determine the preferred form of existence of the oxygen particles, the solutions of the atomic oxygen (O^0), as well as O^- and O^{2-} ions were considered. A possible reaction $2O^- = O^0 + O^{2-}$ was also taken into account, i.e. it was assumed that the dissolution of O_2 in the oxide, which dissociates according to the scheme $O_2 \rightarrow 2O^0$, should be accompanied by an increase in O^- concentration and a decrease in O^{2-} concentration. Charges of iron ions were not changed in this case. The heat of dissolution of oxygen as O^0 (ΔH) was estimated as $\sim 1000 \text{ kJ (mol } O_2)^{-1}$ at 0 K and $768 \text{ kJ (mol } O_2)^{-1}$ at 2000 K. The heat of dissolution of oxygen as O^- was $428 \text{ kJ (mol } O_2)^{-1}$. Since that the dissolution as O^- is preferable. The solubility of O_2 at 1700 K may be described by the expression $X(O^-) = 1.3 \times 10^{-10} p_{O_2}^{1/4}$, where X is the ionic portion of O^- in the oxide and p_{O_2} is the partial pressure of the oxygen expressed in atm. units. The solubility decreases rapidly as temperature decreases.

VII. Simulation of multi-component systems

It was shown by NMR,²⁰⁴ that the aluminium ions in multi-component silicate glasses have tetrahedral coordination at any Al_2O_3 content, while silicon ions have one or two terminal oxygen neighbours. The coordination number for the B–O pairs is mainly 4. In lead-fluoride-silicate glasses, the silicon ions always have two terminal O^{2-} neighbours.

Several complex oxides in $K_2O-Na_2O-SiO_2$, $CaO-Na_2O-SiO_2$, and $B_2O_3-Na_2O-SiO_2$ systems were investigated using the MD method.^{84, 205, 206} It was shown that the inclusion of Na^+ ions leads to destruction of Si–O–Si bonds; Na^+ ions occupy the cavities between 3–8 non-bridging oxygen ions. Small rings are formed and the number of silicon ions with five oxygen neighbours increases. However, when the volume or temperature are increased, the Si ions with $z(\text{Si–O}) = 5$ disappear.

A ‘poly-alkali effect’ caused by a mutual influence of different ions of alkali metals was studied for silicate glasses using the MD method.²⁰⁷ The calculated values of electrical conductivity for the glasses indicate the presence of the effect (a minimum on the plot of conductivity vs. composition). Heating of the system results in a weakening of the effect due to easier relaxation of anions. Preferable ways of diffusion of alkali metal ions in the glass were determined. The application of NMR to structural studies of the alkali- and aluminosilicates including the analysis of the poly-alkali effect were reviewed.²⁰⁸ Alkali metal ion transfer was also studied.²⁰⁹

Models of aluminosilicates, such as $7CaO \cdot Al_2O_3 \cdot 2SiO_2$, $5CaO \cdot Al_2O_3 \cdot 2SiO_2$, $3CaO \cdot Al_2O_3 \cdot 2SiO_2$, $CaO \cdot Al_2O_3 \cdot 2SiO_2$,

were constricted using the MD method at 400 K.²¹⁰ Comparison of the CN values calculated from the PPCF and the characteristics of the Voronoi polyhedra showed that for all pairs, except Ca–O, reasonably good agreement was achieved. The deviations for the Ca–O pairs were due to the formation of clusters of admixturing atoms around the oxygen anions.²¹¹ Structures of $CaO \cdot Al_2O_3 \cdot 2SiO_2$ were studied using the X-ray diffraction and the MD method. It was established that the structures include a framework of fused SiO_4 and AlO_4 tetrahedra and Ca^{2+} ions. The framework contains four- and six-membered rings. The main structural defects resulting in disordering are three- and five-membered rings.

A series of models (1300 atoms in the basic cube) for melts with 10 different compositions in the $NaAlSiO_4-SiO_2$ system at 2500–4500 K and 2–5 GPa was constructed using the MD method.²¹² The run duration was 0.1 ns. The Coulomb interactions were taken into account according to the Ewald method. It appeared that more than 90% of silicon and aluminium ions have CN = 4, and more than 90% of oxygen ions have two neighbouring cations. These results insignificantly depend on temperature. It was established that the T–T coordination (T = Al or Si) depends more on the composition than the T–O coordination. If a model contains more than 1000 ions, the self-diffusion coefficients and conductivity no longer depend on the size of a model; for $N = 400-600$, these characteristics are overestimated by 10%–100%. A cut-off of the Ewald sums additionally distorts the model. The dependence of structure on the number of particles in the model is not so pronounced. The replacement of silicon ions by Al + Na pairs leads to a decrease in the mean T–O–T angle, which is due to the increase in the number of Al–O–Al bridges and the broadening of the azimuthal angle distributions. The PCF oscillations are virtually absent at distances exceeding 500 pm.

MD-models of sodium aluminosilicates with the ratio $a = Al_2O_3/Na_2O = 0.25-2.0$ were constructed.²¹³ At $a = 1$, an extremum of the sodium ion self-diffusion coefficient and its activation energy was observed, it was analogous to that for the viscosity and conductivity. When $a < 1$, the size of rings in the structure decreases, and a minimum concentration of terminal oxygen ions was observed for $a = 1$. When $a > 1$, the groups of neighbouring oxygen particles with $z(O-O) = 3$ appear.

Models of glassy pyrope ($Mg_3Al_2Si_3O_{12}$) and grossular ($Ca_3Al_2Si_3O_{12}$) were constructed using the MD method at 300 K.²¹⁴ Good agreement with the X-ray data on their structure was achieved. The first PPCF peaks for the Si–O and Al–O pairs in pyrope appeared broader than those in grossular. It was found that Al–O–Al combinations were present in the structure, i.e. Al ions do not avoid close proximity to each other. A proportion of Al ions act to modify the network.

Two series of ionic models of MO and MO_2 solutions in non-crystalline $(CaO)_x(SiO_2)_{1-x}$ oxides with $x = 1, 2/3, 1/2, 1/4$, at 0 and 2000 K were constructed using the MD method.²¹⁵ The models corresponded to real and hypothetical oxides. The ratios of the activity coefficients γ_{MO}/γ_{CaO} and $\gamma_{MO_2}/\gamma_{SiO_2}$ were calculated for various x . It was demonstrated that for the MO series the γ_{MO}/γ_{CaO} ratio increases with the increase in the size of M ion for $x > 0.8$ and decreases for $x < 0.8$. This means that for $x > 0.8$ the $CaO-SiO_2$ oxides behave as the basic and for $x < 0.8$ as the acidic ones. However, this rule does not hold for admixtures of the MO type; and neither oxide of the $CaO-SiO_2$ system is neutral in respect of these admixtures. Therefore, the thermodynamic scale of basicity for simple oxides, and hence the meaning of the neutral oxide may be established only for admixtures of a certain type (such as MO) in the $CaO-SiO_2$ system. These scales may differ for different types of admixtures.

Models of an amorphous $(AgI)_x(AgPO_3)_{1-x}$ system for $x = 0-0.5$ were constructed using the Reverse MC method and data on neutron and X-ray diffraction together with X-ray absorption fine structure (EXAFS).^{216, 217} For the initial configuration, it was assumed that PO_4 tetrahedra are linked in a chain via two bridging oxygen ions of each tetrahedron and the chains

are linked through the silver ion and two terminal oxygen ions. The number of ions in the basic cube was 3840–5376. Reasonably good agreement between the experimental and simulated structural factors and EXAFS spectra was achieved. No AgI microcrystals were found in the models. It was established that the iodide admixtures are situated in the pores of the phosphate network. The size of pores decreases with a decrease in the AgI concentration. It was shown that the first distinct peak in the total structural factor is due to density correlations of the phosphate network, which increase with the addition of iodide, rather than due to the distribution of the AgI admixtures. The concentration of the tunnel-shaped pores passes the percolation threshold in the range $0.2 < x < 0.3$, that provides rapid diffusion of Ag^+ ions, and the structure acquires the superionic conductivity.

A model of $(\text{AgI})_x(\text{Ag}_2\text{O} \cdot 2\text{B}_2\text{O}_3)_{1-x}$ glass (960 particles in the basic cube, $x = 0.1$ and 0.6) was constructed using the BMH pair potentials.²¹⁸ It was demonstrated that the calculated structural factor of the model has a peak in the small angle region at 9 nm^{-1} (detected earlier by the neutron scattering), which is due to correlations in arrangement of AgI clusters embedded into the boron-oxygen network. Addition of AgI up to $x = 0.6$ does not affect the structure of the boron-oxygen framework.²¹⁹ In the case of $(\text{LiCl})_x(\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3)_{1-x}$ glass ($x = 0$ and 0.6), the addition of chloride leads to a decrease in $z(\text{B}-\text{O})$, which finally results in a more open boron-oxygen framework and lower structural ordering. The boron-oxygen network is composed mainly of statistically linked BO_3 and BO_4 groups. Glasses with overall composition $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{NaCl}$ were investigated by the MD method.²²⁰ The effects of separation of phases in the glass were successfully reproduced within the atomic model.

VIII. Simulation of ion transfer processes

A parameter such as electrical conductivity, which is sensitive to the bonding type, is a useful tool to examine the adequacy of the ionic model. In the case of covalent bonding, the oxide should be a dielectric. For the cases of mixed ionic/covalent bonding, it is very difficult to use the computational methods to estimate the electrical conductivity while this can be easily estimated within the ionic model. To this end, it is necessary to consider the forces of external field given by the eEz_i term, where E is the external electric field in the summation of all forces applied to an atom. In MD-simulation, it is necessary to calculate the charge flows for each type of ion in the direction of E and their sum, which is the current. Reliable averaging of the data is needed due to strong fluctuations of the flows. Another point is that the ion transfer cannot be examined in rather weak fields comparable with those normally used in practice. The electric field of the order of $10^8-10^9 \text{ V m}^{-1}$ corresponds to the electric force making a noticeable drifting flow. Substantial structural distortions of the melt occur in stronger electric fields. Nevertheless, calculations of the conductivity for models of oxide systems are a good test for the adequacy of the ionic concept.

The study of processes of the ion transfer in electric fields at 2000 K for oxides in the $\text{CaO}-\text{SiO}_2$ system showed that the mechanism of ion transfer is drifting.²²¹ The values of the calculated conductivity are in good agreement with the experimental data for melts with conductivity higher than $50 (\text{Ohm m})^{-1}$ (for CaO concentration exceeding 65 mol.%). For systems with the conductivity below $10-20 (\text{Ohm m})^{-1}$ the accuracy of the computational methods is not sufficient. The effect of 'removal' of Si^{4+} ions by surrounding O^{2-} ions was found. Therefore, the Si^{4+} ions give a negative contribution to the total conductivity. The reason for this effect is the high stability of the complex SiO_4^{4-} ions.

IX. Conclusion

All data considered above show that for many oxide systems (except for phosphate and several other) the ionic model allows

one to obtain results that are in reasonably good agreement with the experimental data on the thermodynamic, structural, diffusion, and electrochemical (mobility in the electric field) properties. Good results were obtained even using such simple interparticle potentials, as the Born–Meyer potential. Complicated modifications of the potential describe certain objects with higher precision, but make the prediction of properties of complex systems based on data for the simpler ones more difficult.

The prediction of the vibrational spectra on the basis of simple ionic model is not so confident. The agreement with the experimental IR and Raman spectra is more difficult to achieve. Therefore, these properties were not considered here. Further investigations are needed in this field. Nevertheless, the results discussed show that clear understanding of the structural features and properties of non-crystalline oxide systems may be achieved by a combination of experimental and computer simulation methods.²²²

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Radiation chemistry of aqueous solutions of actinides

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Abstract. The data on radiolytic transformations of ions of uranium, neptunium, plutonium, americium, curium and transcurium elements in aqueous solutions are generalised. The results of studies on the kinetics of fast reactions of these ions with primary products of water radiolysis (hydrated electron e_{aq}^- , H, OH, and O^- radicals and H_2O_2), many inorganic (Cl_2^- , NO_3^- , SO_4^{2-} , CO_3^{2-} , O_3^- etc.) and organic free radicals are analysed. The mechanism of γ - and α -radiolysis of solutions of actinide ions is discussed. The bibliography includes 183 references.

I. Introduction

Aqueous solutions of actinides are widely used in nuclear power engineering and radiochemical industry. Firstly, many systems meant for processing of nuclear materials are aqueous solutions. When these solutions are highly radioactive, actinide ions can undergo various radiolytic transformations induced by the radiation from the radionuclides present. It is clear that this can markedly influence technological processes.

Secondly, actinide ions are present in radioactive wastes (including highly radioactive liquid wastes). It is obvious that the knowledge of the regularities of radiation-induced chemical processes involving these ions is needed to correctly solve the problems of prolonged storage and disposal of these wastes: to store liquid wastes in tanks or to dispose of them in deep geological formations, to develop a technology for isolation of α -nuclides from wastes and to carry out this isolation, to dissolve plutonium-containing precipitates, etc.

Thirdly, in the case of accidents at nuclear power plants, radionuclides (fission-product elements, plutonium, etc.) can get into water; in those places where these elements are concentrated, radiolytic transformations of actinide ions can occur. These transformations may have an influence on the behaviour of

actinides in the environment, and this should be taken into account in radioecological investigations.

Actinide ions can exist in aqueous solutions in a variety of oxidation states (for example, the oxidation number of americium varies from two to seven); therefore a wide range of radiation-induced redox reactions can be studied.

The radiation chemistry of aqueous solutions of actinide ions has been developed since the mid-1940s; its development started soon after the discovery of plutonium.¹ Early studies dealt with radiolysis of aqueous solutions of plutonium induced by its own α -radiation; later, radiolysis under the action of external ionising radiation (X-rays) was also investigated. Somewhat more recently, first studies dealing with the radiation chemistry of aqueous solutions of americium, uranium and neptunium ions were accomplished (see, for example Ref. 1). It should be noted that in the majority of these studies, the occurrence of a certain radiolytic transformation has been detected only qualitatively. The mechanisms of these transformations have been studied since the 1960s. Significant progress along this line has been achieved by virtue of the method of pulse radiolysis with fast recording of short-lived species (this method is described in detail in two monographs^{2,3}). The results obtained up to 1980 are summarised in Ref. 1.

The present paper surveys the current state of the radiation chemistry of aqueous solutions of actinides. It is largely based on the data published during the past 15 years. The results obtained before 1980 have been surveyed in monographs^{1,4} and in a handbook.⁵ However, in some cases, to make the presentation more complete, some earlier studies are also discussed. This is done when their results need to receive a different interpretation due to the appearance of new information. In addition, published data on the radiolysis of solutions of actinides in nitric acid are considered in detail, because these systems are important from the practical viewpoint.

II. General information about the mechanism of radiolysis of water

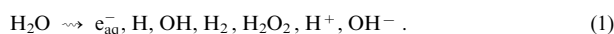
Studies of aqueous solutions (including solutions of actinides) in radiation chemistry are based on the following views on the mechanism of radiolysis of water.^{1,6} The primary products formed in this process are the hydrated electron e_{aq}^- , a hydrogen atom, an OH radical (its dissociated form is the O^- radical ion), molecular hydrogen H_2 , hydrogen peroxide (its dissociated forms

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are HO_2^- and O_2^{2-}) and H_{aq}^+ and OH^- ions. This can be written as follows



The radical species formed in the radiolysis (e_{aq}^- , H, and OH) as well as hydrogen peroxide enter into various reactions with dissolved compounds (evidently, including actinide ions) and thus cause various radiolytic transformations of the latter.[†]

In dilute aqueous solutions (in which concentrations of solutes are up to $\sim 10^{-3}$ – 10^{-2} mol litre⁻¹), the radiation yields of the above primary products of radiolysis of water hardly depend on the concentration of the solution. The respective values for γ -radiation and for high-energy electrons are listed in Table 1.

Table 1. Radiation yields of the products ^a [molecule (100 eV)⁻¹] of water radiolysis induced by γ -radiation of ⁶⁰Co and by high-speed electrons with an energy of 1 MeV or higher.^{1,6}

pH	$G_{e_{\text{aq}}^-}$	G_{H}	G_{OH}	G_{H_2}	$G_{\text{H}_2\text{O}_2}$	$G_{\text{H}_{\text{aq}}^+}$	G_{OH^-}
0–2	3.05	0.6	2.95	0.45	0.8	—	—
4–9	2.8–2.9	0.6	2.8–2.9	0.45	0.75	3.3–3.4	0.5–0.6
12–13	3.05	0.55	2.9	0.4	0.75	—	—

^a Radiolysis of water also affords oxygen atoms; however, their yield is negligibly small.

In concentrated solutions, these yields do depend on the concentration, because the solute can react with the primary products in ‘spurs’ and tracks. In addition, the ‘direct’ influence of the ionising radiation on the substance becomes apparent in these solutions. It also cannot be ruled out that excited water molecules are involved in radiolytic transformations.

Actinides emit α -particles with an energy of 5–6 MeV; having passed through a material (including water), these particles form cylindrical tracks with high concentrations of primary products of radiolysis. Consequently, the yields of the latter differ markedly from those obtained in the case of γ -irradiation or irradiation with high-energy electrons. The yields of products formed upon the action of α -particles emitted by actinides have not been determined. They were measured for the α -particles with an energy of 5.3 MeV emitted by ²¹⁰Po (Table 2). The yields of products

Table 2. The yields of primary products of water radiolysis induced by α -particles.

Energy/ MeV	Medium ^a		$G_{e_{\text{aq}}^-} + G_{\text{H}}$		G_{OH}	G_{H_2}	$G_{\text{H}_2\text{O}_2}$	G_{HO_2}	Ref.
	I	II							
5.3	H ₂ SO ₄	0.4	0.55	0.35	1.4	1.3	0.2	7	
6.4		(7)	—	0.4	—	0.95	0.085	8	

^a Here and in the other Tables, the following designations are used: I — aqueous solution; II — concentration of the solution in M; the number in parentheses — pH of the medium.

obtained upon the action of α -particles with an energy of 6.4 MeV were also included in the Table. Comparison of the data presented in Tables 1 and 2 indicates that in the case of α -particles, the yields of the radical products of water radiolysis decrease, while those of the molecular products increase. Another specific feature is that HO_2 radicals (or O_2^- as the dissociated form) are formed in a relatively high yield among the primary products.

[†] In this review, the radiation yields of the primary products of water radiolysis are denoted by the letter G , the corresponding product being shown as the subscript (for example, $G_{e_{\text{aq}}^-}$); the overall yield of a product (with allowance for secondary reactions) is symbolised by the letter G with the product given in parentheses; the yield of the consumption of a species, for example U(IV), is denoted by $G[-\text{U(IV)}]$ and the yield of its formation is written as $G[\text{U(IV)}]$.

When the concentration of actinides in a solution is relatively high, their α -radiation is fairly intense. This can lead to radiolytic transformations of the solutes (including actinides). Radiolysis of actinides induced by their own α -radiation is referred to as self-radiolysis.

III. The reactivity of actinides in aqueous solutions

The radiation-induced chemical processes involving actinide ions in solutions comprise their interaction with primary products of water radiolysis and with inorganic and organic free radicals resulting from the radiolysis as well as the reactions of actinide ions in unstable oxidation states (arising upon radiolytic reduction or oxidation) with stable compounds present in the solution. Rate constants for these processes have been measured by various methods;^{9–13} the method of pulse radiolysis with spectrophotometric recording of short-lived species has been used most often. In some cases, conductometric recording has been employed. Some rate constants have been estimated by computer modelling of radiolytic processes.

1. The reactivity of actinide ions towards the primary products of radiolysis of water

Numerous studies have dealt with the kinetics of reactions of actinide ions with the primary products of water radiolysis. The rate constants for the reactions of uranium, neptunium, plutonium, americium, berkelium and californium ions with hydrated electrons, H, OH and O^- radicals and with hydrogen peroxide have been determined.

a. Reactions with the hydrated electron

The rate constants of the reactions of actinide ions with e_{aq}^- in acidic, nearly neutral, carbonate-containing and alkaline media are listed in Table 3. The reactions of the hydrated electron with tetra-, penta-, hexa- and heptavalent actinides (An) have large rate constants (from $\sim 2 \times 10^9$ to $\sim 1 \times 10^{11}$ litre mol⁻¹ s⁻¹). The rates of the majority of these reactions are diffusion-controlled. As in the case of other diffusion-controlled reactions, there is no correlation between the rate constants and the redox potentials E° of the corresponding pairs of actinide ions, although the extreme values of E° differ by ~ 2 V, and the redox potential of the U(IV)/U(III) pair is -0.6 V.^{21,34–39} A noticeable shift of the potential to the negative region observed for Th(IV) and Am(III) ions results in a decrease in the rate constants.

The reaction rates are ‘insensitive’ to the change in the formal charge and in the number of water molecules in the equatorial plane of the actinide ion. This can be seen in the case of complex ions of hexavalent uranium: $\text{UO}_2(\text{H}_2\text{O})_n^{2+}$, $\text{UO}_2(\text{H}_2\text{O})_{n-1}\text{OH}^+$, $\text{UO}_2(\text{IMDA})$, $\text{UO}_2(\text{NTA})^-$, $\text{UO}_2(\text{C}_2\text{O}_4)_2^{2-}$, and $\text{UO}_2(\text{CO}_3)_3^{4-}$. The rate constants for all these ions are close to one another.

The decrease in the charge of tetravalent actinide ions in solutions containing sulfuric acid also has no significant influence on the rate constants. The formation of AnSO_4^{2+} ions may not be accompanied by an increase in the electron density in the orbitals of the actinide ion accepting an electron.

Schmidt *et al.*²⁸ have studied the mechanism of reduction of pentavalent neptunium ions with hydrated electrons in a weakly acidic medium using pulse radiolysis with conductometric recording of short-lived species. They obtained results indicating that at pH 3.6–5.8, the reduction of NpO_2^+ to $\text{Np}(\text{OH})^{3+}$ occurs *via* the intermediate formation of $\text{NpO}_2 \cdot 6\text{H}_2\text{O}$, $\text{Np}(\text{OH})_4 \cdot 4\text{H}_2\text{O}$, $\text{Np}(\text{OH})_3^+$ and $\text{Np}(\text{OH})_2^{2+}$. The rate constant for the transformation of $\text{NpO}_2 \cdot 6\text{H}_2\text{O}$ into $\text{Np}(\text{OH})_4 \cdot 4\text{H}_2\text{O}$ is 1.5×10^6 s⁻¹, while the rate constants for the protonation of $\text{Np}(\text{OH})_4$, $\text{Np}(\text{OH})_3^+$ and $\text{Np}(\text{OH})_2^{2+}$ are 3.75×10^{10} , 4.0×10^{10} , and 4.28×10^{10} litre mol⁻¹ s⁻¹, respectively. These researches also determined the p*K* values for the equilibria between NpO_2OH and NpO_2^+ , $\text{Np}(\text{OH})_2^{2+}$ and $\text{Np}(\text{OH})_3^+$. They were equal to 8.7 and 4.5, respectively.

Table 3. Rate constants for the reactions of actinide ions with the hydrated electron.

Actinide	Medium		$10^{-10} k$ /litre mol ⁻¹ s ⁻¹	Ref.	Actinide	Medium		$10^{-10} k$ /litre mol ⁻¹ s ⁻¹	Ref.
	I	II				I	II		
Th ⁴⁺	Weakly acidic solution	—	1.9	14	Np(VI)	OH ⁻	5.0	2.0	24, 25
	HClO ₄	0.01	< 0.01	15		OH ⁻	7.5	1.1	24, 25
ThSO ₄ ²⁺	Weakly acidic solution	—	1.1	14		OH ⁻	10.0	0.83	24, 25
						OH ⁻	12.5	0.68	24, 25
U(VI)	Acidic solution	—	7.4	16	Np(V)	—	(5.3)	1.97	17
	—	(5.3)	1.73	17		—	(6.1)	2.13	17
	—	(6.8)	1.25	17	Np(V), carbonate	CO ₃ ²⁻	0.1	0.25	27
	—	(2.9)	1.7–7.4	18, 19		CO ₃ ²⁻	1.0	0.20	27
	—	(9.6)	0.45	18	Np(V) complex	CO ₃ ²⁻	5.0	0.19	27
	Artificial sea water	—	2.12	20		OH ⁻	1.0	0.50	24, 25
						OH ⁻	2.0	0.61	24, 25
						OH ⁻	5.0	0.59	24, 25
						OH ⁻	7.5	0.31	24, 25
U(VI), complex with	IMDA	0.01 (10.5)	1.93	20	Np(IV)	HClO ₄	0.023	6.3	15
	IMDA	0.05 (8.0)	3.87	20		HClO ₄	0.038	6.3	15
IMDA	IMDA	0.25 (8.0)	3.10	20		HClO ₄	0.055	6.0	15
U(VI), complex with	NTA	0.01 (9.0)	1.67	20		HClO ₄	0.91	6.5	15
	NTA	0.05 (9.5)	1.90	20		H ₂ SO ₄	0.042	7.0	15
NTA	NTA	0.25 (9.0)	2.41	20		H ₂ SO ₄	0.06	6.1	15
U(VI), oxalate complex	C ₂ O ₄ ²⁻	0.01 (5.0)	2.75	20		H ₂ SO ₄	0.68	5.8	15
					Np(IV), carbonate complex	CO ₃ ²⁻	0.1	0.5	27
U(VI), carbonate complex	CO ₃ ²⁻	0.01 (11.4)	1.32	20		CO ₃ ²⁻	1.0	0.4	27
	CO ₃ ²⁻	0.05	1.18	21		CO ₃ ²⁻	4.3	0.4	27
						CO ₃ ²⁻	6.0	0.3	29
U(IV)	HClO ₄	0.05	6.8	22	Pu(VII)	OH ⁻	1.0	3.5	24
	HClO ₄	0.1	6.5	22, 23		OH ⁻	2.0	4.2	24
	HClO ₄	1.0	10.0	22		OH ⁻	5.0	2.3	24
	H ₂ SO ₄	0.68	5.8	15		OH ⁻	7.5	2.0	24
Np(VII)	OH ⁻	0.1	2.9	24, 25	Pu(VI)	—	(5.6)	6.44	17
	OH ⁻	0.5	3.2	24, 25		—	(6.1)	5.76	17
	OH ⁻	1.0	2.0	24, 25	Pu(VI), carbonate complex	CO ₃ ²⁻	0.05	2.28	21
	OH ⁻	2.0	2.1	24, 25		CO ₃ ²⁻	0.1	2.3	27
	OH ⁻	5.0	1.7	24, 25		CO ₃ ²⁻	1.0	1.4	27
	OH ⁻	7.5	1.3	24, 25		CO ₃ ²⁻	5.0	0.68	27
	OH ⁻	10.0	0.88	24, 25	Pu(VI)	OH ⁻	2.0	1.9	24
	OH ⁻	12.5	0.7	24, 25		OH ⁻	5.0	2.0	24
Np(VI)	—	(5.3)	6.32	17		OH ⁻	7.5	0.66	24
	—	(5.8)	5.43	17	Pu(IV)	H ₂ SO ₄	0.018–0.033	3.3	15
	—	(2.5)	10.0	26		H ₂ SO ₄	0.078	12	15
NpO ₂ OH ⁺	—	—	2.9	26	Pu(IV), carbonate complex	CO ₃ ²⁻	6.0	0.3	29
Np(VI), carbonate complex	CO ₃ ²⁻	0.05	2.34	21					
	CO ₃ ²⁻	0.1	1.9	27	Am(VI)	LiClO ₄	0.11 (5.3)	3.11	30
	HCO ₃ ⁻ + CO ₃ ²⁻	0.5 + 0.5	1.8	27		LiClO ₄	0.11 (6.0)	3.9	30
						LiClO ₄	0.11 (5.2)	2.8	30
	CO ₃ ²⁻	1.0	1.2	27	Am(V)	LiClO ₄	0.11 (6.0)	3.18	30
	CO ₃ ²⁻	5.0	0.62	27		LiClO ₄	0.11 (5.8)	2.45 × 10 ⁻²	30
Np(VI)	OH ⁻	0.5	2.3	24, 25	Am(III)	—	(~ 6.0)	~ 3 × 10 ⁻²	31
	OH ⁻	1.0	1.3	24, 25	Bk(III)	—	(5.0)	1.12 × 10 ⁻¹	32
	OH ⁻	2.0	1.2	24, 25	Cf(III)	—	(5.1–5.3)	≥ 3 × 10 ⁻¹	33

Note. The following designations are used: IMDA — iminodiacetate, NTA — nitrilotriacetate.

When Np(V) is reduced to Np(IV), the structure of the neptunium ion changes (from NpO₂⁺ to Np⁴⁺), and this can significantly hamper the reaction. Nevertheless, the reaction rate in an acid medium is close to its diffusion limit. Therefore, it was suggested²⁸ that the electron transfer in this reaction is a non-adiabatic process, which yields Np(IV) in an electronically excited state as an intermediate product having an ‘inappropriate’ electronic configuration. Then this configuration rearranges into the configuration corresponding to a hydrolysed ion of tetravalent neptunium.

The rates of the reactions of e_{aq}⁻ with tetravalent uranium, neptunium and plutonium in acidic media or with heptavalent

neptunium and plutonium in alkaline solutions are most probably larger than the diffusion limit. This is due to a tunnel mechanism of these reactions (detailed information about the tunnel mechanism of reactions of e_{aq}⁻ can be found in a monograph⁴⁰).

In a carbonate-containing medium, the rate constants for the reactions of the hydrated electron with An(VI) depend only slightly on the concentration of carbonate ions. It has been concluded that the reaction rates are limited by the diffusion of the reacting species.²⁷ It was also suggested that the composition of the AnO₂(CO₃)₃⁴⁻ complex ions does not change over the studied ranges of concentrations of carbonate ions. Therefore, variation of

the carbonate concentration influences the reaction rate only to the extent to which it changes the viscosity of the medium.

The rate constant for Np(V) is approximately an order of magnitude lower than that for Np(VI). This is due to the fact that the transition of Np(V) into Np(IV) is accompanied by a structural rearrangement.²⁷ The influence of the concentration of carbonate ions on the reaction rate in the case of Np(V) is also slight. It was noted that in this case, too, ion diffusion is the crucial factor.²⁷ The reaction of e_{aq}^- with Np(IV) occurs faster than the corresponding reaction with Np(V). This is due to the fact that Np(IV) is converted into Np(III) without a change in the structure.

The rate constants for the reactions of actinides with the hydrated electron in dilute alkaline solutions differ only slightly from those in weakly acidic solutions. The reaction rates decrease markedly at $[OH^-] \geq 7.5$ M. Several possible reasons for the decrease in the reaction rates in concentrated alkaline solutions have been proposed.²⁴ They include an increase in the viscosity of these solutions, capture of electrons in deeper traps, the formation of pairs of the $M^+ \dots e_{aq}^-$ type (M^+ is an alkali metal cation) and the change in the activity coefficients of ions at high ionic strengths.

b. Reactions with a hydrogen atom

The reactions of actinide ions with hydrogen atoms are significant in acidic solutions. In these solutions, the hydrated electron reacts with H^+ being thus converted into an H atom. This reaction is fast: $k = 2.4 \times 10^{10}$ litre mol⁻¹ s⁻¹ for solutions with pH 2.1–6.⁵ The reaction of an actinide ion with e_{aq}^- in an acidic medium is possible in the case where the product of the rate constant for the reaction of the actinide ion with the hydrated electron by the actinide concentration is comparable with the product of the rate constant for the reaction of e_{aq}^- with H^+ by the concentration of the latter. In neutral media, the reactions of H atoms are less significant because the role of the interaction of e_{aq}^- with H^+ is low and the radiation yield of H amounts to ~20% of the yield of e_{aq}^- (see Table 1). In alkaline media, processes involving H barely occur, because this species reacts with OH^- to give a hydrated electron.

The rate constants for the reactions of An(VI), An(V) and An(IV) with H are markedly lower than those for the corresponding reactions with the hydrated electron. This can be seen from the comparison of the data presented in Tables 3 and 4.

This difference can be explained by the fact that the redox potential of the H atom (–2.3 V) is less negative than that of e_{aq}^- (–2.87 V).⁶ The difference between the reaction mechanisms also plays a certain role. The mechanism of the interaction of e_{aq}^- with any ion consists in electron transfer. The reactions of the H atom apparently involve the water incorporated in the hydration shell of the ion. It cannot be ruled out that this reaction starts with the

Table 4. Rate constants for the reduction of actinide ions with H atoms in aqueous solutions.

Actinide	Medium		$10^{-6} k$ /litre mol ⁻¹ s ⁻¹	Ref.
	I	II		
U(VI)	HClO ₄	1.0	45	41
	H ₂ SO ₄	0.5	7	42
U(IV)	H ₂ SO ₄	1.0	< 1	42
Np(VI)	HClO ₄	1.0	400	42
	—	(1.0)	< 1	26
Np(V)	HClO ₄	1.0	< 5	41
Np(IV)	HClO ₄	0.9	< 1	42
Pu(VI)	HClO ₄	1.0	200	42
	H ₂ SO ₄	0.6	45	42
Pu(IV)	HClO ₄	3.0	17	42
	H ₂ SO ₄	1.6	61	42
Am(VI)	Solution of perchloric acid	—	1600	43
Am(V)	HClO ₄	1.0	200	43

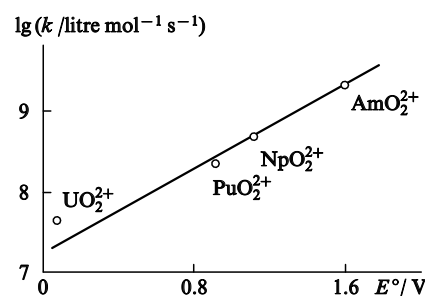


Figure 1. Dependence of the rate constants for the reactions of H atoms with actinyl ions in a 1 M solution of HClO₄ on the redox potentials of the AnO₂²⁺/AnO₂⁺ pairs.

insertion of H into a water molecule to give H₃O, and then electron transfer from H₃O to the central ion occurs.

The dependences of the logarithms of the rate constants for the reactions of H with all the AnO₂²⁺ ions studied on the redox potentials of the AnO₂²⁺/AnO₂⁺ pairs (or on the free energy of the reaction) are nearly linear (Fig. 1). Thus, the mechanisms of these reactions are identical and their rates are not controlled by diffusion. However, since there are no data on the rate of the exchange of water molecules coordinated by actinyl ions, this mechanism cannot be interpreted in detail.

For the reactions of actinyl ions with H, no linear correlation between the logarithm of the rate constant and the E° value is observed. It should also be noted that the rate constants for the reactions of H with NpO₂⁺ and AmO₂⁺ differ by two orders of magnitude, although the difference between the E° values for the Np(V)/Np(IV) and Am(V)/Am(IV) pairs is not that large.

The reactions considered above are reduction processes. Oxidation by H atoms is also known; for example, it reacts with U(V), Np(III) and Pu(III). The rate constants for these reactions are presented in Table 5. It can be seen that on passing from a solution in perchloric acid to a solution in sulfuric acid the rate constants for Pu(III) and Np(III) increase. This is due to the fact that the redox potential of the An(IV)/An(III) pair in sulfuric acid is smaller than that in perchloric acid and the potential of the Np(IV)/Np(III) pair is also smaller. In the case of U(V), the nature of the acid has apparently no influence on the rate of the process.

Table 5. Rate constants for the oxidation of actinide ions with H atoms in aqueous solutions.^{42, 44}

Actinide	Medium		$10^{-6} k$ /litre mol ⁻¹ s ⁻¹
	I	II	
U(V)	HClO ₄	0.1	~400
	H ₂ SO ₄	0.4	10–400
Np(III)	HClO ₄	1.0	63
	H ₂ SO ₄	1.0	190
Pu(III)	HClO ₄	3.0	< 1
	HClO ₄ + H ₂ SO ₄	0.2 + 1.8	6

Evidently, oxidation with an H atom is not an elementary process. It may involve the intermediate formation of a hydride ion as has been observed for the oxidation of Fe²⁺ ions (see, for example, Ref. 6).

c. Reactions with OH and O⁻ radicals

The OH radical exists in acidic, neutral and weakly alkaline media.

In an alkaline medium, electrolytic dissociation affords the O⁻ radical ion. The pK value for the corresponding equilibrium is 11.9 (see, for example, Ref. 6). The rate constant for the OH + OH⁻ reaction is large,⁵ 1.2×10^{10} litre mol⁻¹ s⁻¹; therefore, at pH > 13, it is the O⁻ radical ion that reacts with dissolved

Table 6. Rate constants for the reactions of actinide ions with OH radicals in aqueous solutions.

Actinide	Medium		$10^{-8} k$ /litre mol ⁻¹ s ⁻¹	Ref.
	I	II		
U(III)	Acidic	—	4.1	45
U(IV)	HClO ₄	0.1	9.2	22, 46
	HClO ₄	1.0	8.6	22, 46
Np(III)	HClO ₄	1.0	40	47
Np(IV)	HClO ₄	1.0	3.2	48
Np(V)	HClO ₄	(2.52–2.95)	5.7	48
	HClO ₄	0.1	4.4	48
	HClO ₄	1.0	4.3	48
	—	(< 4.0)	0.43	26
	—	(4.75)	2.7	49
	—	(4.23)	5.9	49
	—	(3.64)	4.2	49
	HClO ₄	0.1	5.8	49
	HClO ₄	1.0	4.2	50
	—	(4.0)	18.3	51
Pu(IV)	HClO ₄	3.0	2.4	47
Am(III)	—	(4.0)	3.2	52
	—	(2.0)	3.4	52
	—	(1.0)	11.0	52
	HClO ₄	1.0	16.0	52
	LiClO ₄	0.11, (5.1)	4.1	29

substances including actinides in dilute solutions (with concentrations of no more than $\sim 10^{-3}$ mol litre⁻¹).

The results of studies on the kinetics of the reactions of OH with An(III), An(IV) and An(V) and the reactions of O⁻ with An(V) and An(VI) are presented in Tables 6 and 7. The rate constants of these reactions do not depend on the redox potentials of the Anⁿ⁺¹/Anⁿ pairs; for example, the potentials of the U(IV)/U(III) and Am(IV)/Am(III) pairs are -0.52 and 2.62 V, respectively, whereas the rate constants for the reactions of U(III) and Am(III) are 4.1×10^8 and 3.4×10^8 litre mol⁻¹ s⁻¹ (Table 6). Structural rearrangements also have no influence on the reaction rate [oxidation of Np(IV) and Np(V) provide an example]. It is noteworthy that on passing from a weakly to a strongly acidic medium the rate constant of the reaction of OH with Pu(III) decreases about four-fold, whereas the rate of a similar reaction with Am(III) increases by the same factor.

Table 7. Rate constants for the reactions of penta- and hexa-valent neptunium ions with O⁻ radical ions in aqueous solutions of LiOH.^{53, 54}

Ion	[LiOH] ^a	$10^{-7} k^b$	Ion	[LiOH] ^a	$10^{-7} k^b$
Np(V)	1.0	47	Np(VI)	1.03	4.2
Np(VI)	0.033	8.0		1.72	4.2
	0.072	5.4		2.0	5.1
	0.24	3.6		0.5–1.7	6.1
	0.51	4.2		(in NaOH)	

^a Concentration is expressed in mol litre⁻¹, ^b k — in litre mol⁻¹ s⁻¹.

Two possible mechanisms for the oxidation with OH radicals have been proposed. According to one of them, the reaction rate is limited by abstraction by the OH radical of an H atom from a water molecule in the hydration shell of the ion, as has been postulated by Berdnikov⁵⁵ for transition metal ions in general. According to the other mechanism, the radical adds to an actinide ion, and after that, a rearrangement in its inner shell occurs, which is accompanied by the elimination of OH⁻. The latter mechanism was proposed by Golub *et al.*⁴⁵ and supported by Lierse *et al.*⁵¹

d. Reactions with hydrogen peroxide

Hydrogen peroxide can act, with respect to actinide ions, both as an oxidising and a reducing agent. This depends on the pH of the

Table 8. Rate constants for oxidation of actinide ions with hydrogen peroxide in aqueous solutions.

Actinide	Medium		k /litre mol ⁻¹ s ⁻¹	Ref.
	I	II		
U(III)	HClO ₄	0.5	2×10^5	45
U(IV)	HClO ₄	1.0	3.88	56
	H ₂ SO ₄	0.98	1.62	56
	H ₂ SO ₄	0.4	0.41	57
	HCl + NaCl	0.05 + 1.95	23.3	58
	HCl + NaCl	0.1 + 1.9	8.0	58
	HCl + NaCl	0.25 + 1.75	2.4	58
	HCl + NaCl	0.316 + 1.684	1.9	58
	HCl + NaCl	0.5 + 1.5	1.1	58
	HCl + NaCl	1.0 + 1.0	0.45	58
	HCl + NaCl	1.5 + 0.5	0.3	58
	HCl + NaCl	0.5 + 1.5	0.24	58
U(V)	Acidic solution	—	55	59
Np(III)	Solution of perchloric acid	—	30–38	56
Np(IV)	Solution of nitric acid	—	0.08	60
Np(V)	HNO ₃	7.5	0.45 ^a	61
Pu(III)	Solution of sulfuric acid	—	0.055	62

^a Estimated from a figure presented in Ref. 61.

solution and on the redox potential of the actinide pair in this solution. Recall that depending on the pH, hydrogen peroxide exists as H₂O₂, HO₂⁻ (the pK value for the corresponding equilibrium is 11.9⁶) or O₂²⁻ (this ion is formed at pH > 13.5). The rate constants for the oxidation of actinide ions with hydrogen peroxide in aqueous solutions are presented in Table 8.

Comparison of the rate constants with the redox potentials of the corresponding pairs of actinide ions shows a clear-cut tendency for the constants to decrease upon an increase in the potentials. This, in principle, may attest to an outer-sphere mechanism of these processes. However, the oxidation of Np(III) results in the accumulation of Np(V), *i.e.* a two-electron process occurs, and only after some period, Np(IV) appears in the solution as a result of the reaction between Np(III) and Np(V).

Table 8 presents the rate constant for the bimolecular oxidation of Pu(III); however, in a large number of experiments,⁶² the reaction rates were described by the equation:

$$-\frac{d[\text{Pu(III)}]}{dt} = k[\text{Pu(III)}]^2[\text{H}_2\text{O}_2]. \quad (2)$$

The researchers cited⁶² believe that the mechanism of this reaction includes the formation of a peroxide complex, which slowly decomposes to give Pu(IV).

Oxidation of An(IV) is a single-electron process yielding An(V) and OH. This is confirmed by the fact that the oxidation of U(IV) by hydrogen peroxide in a solution saturated with benzene gives rise to phenol.⁵⁷ Oxidation of An(V) in acidic solutions affords only An(VI) and OH. However, it should be noted that during γ -radiolysis in an alkaline solution, Np(V) reacts with hydrogen peroxide to give a peroxo-complex.⁶³

The reduction of actinide ions with hydrogen peroxide results in the formation of HO₂ in addition to the reduced ions. Apparently, the reduction involves intermediate formation of a peroxo-complex.

The rate constants for the reduction of actinide ions with hydrogen peroxide in aqueous solutions are listed in Table 9. Their magnitudes increase with an increase in the difference between the redox potentials of the actinide pair and O₂/H₂O₂. This regularity is especially typical of Pu(IV). The difference between the formal potentials of the Pu(VI)/Pu(V) and O₂/H₂O₂ pairs in an acidic medium is 0.24 V, while that for the same reagent in a solution of NaHCO₃ is 0.15–0.20 V; the corresponding rate constants differ by 4 orders of magnitude. The formation of peroxo-complexes mentioned above also has some influence on the reaction rate.

Table 9. Rate constants for reduction of actinide ions with hydrogen peroxide in aqueous solutions.

Actinide	Medium		k /litre mol ⁻¹ s ⁻¹	Ref.
	I	II		
U(VI)	—	(5.2)	1.39×10^4 (see ^a)	17
Np(VII)	—	(8.7)	4.0×10^4	64
	—	(10.0)	6.2×10^4	64
	—	(12.4)	2.4×10^3	64
	LiOH	0.1, (12.86)	5.8×10^2	64
Np(VI)	LiOH	1.0, (13.7)	3.7×10^2	64
	—	(9.2)	5.0×10^4	64
	—	(10.0)	2.1×10^4	64
	—	(11.0)	4.0×10^3	64
	LiOH	0.1, (12.86)	9.5×10^2	64
	LiOH	1.0, (13.7)	1.4×10^2	64
	Solution of perchloric acid		4.45	56
	Weakly acidic solution		5.9×10^5	17
Np(V)	HNO ₃	7.5	2.2×10^{-1} (see ^b)	61
	HNO ₃	4.5	2.5×10^{-2}	65
	HNO ₃	6.0	3.5×10^{-2}	61
	HNO ₃	7.5	7.7×10^{-2}	61
	HNO ₃	8.4	8.9×10^{-2}	61
Pu(VI)	HClO ₄	1.0	3.2×10^{-3}	56
	HNO ₃	1.0	6.2×10^{-3}	56
	H ₂ SO ₄	0.18	3.1×10^{-3}	56
	NaHCO ₃	0.05	7.0×10^3 (see ^a)	66
	NaHC ₃	0.05	~ 50	66
Pu(IV)	HClO ₄ + Na ₂ SO ₄	0.3 + 0.4	16.0 (see ^c)	67
	HClO ₄	1.0	8.64×10^5 (see ^d)	68
Pu(IV), ^f	HClO ₄	1.5	2.25×10^{-4} (see ^e)	69
Pu(IV)	HNO ₃	0.98–1.96	1.0×10^{-1}	70
Am(VI)	HClO ₄	0.98	1.92×10^4	71
Am(V)	HClO ₄	0.1	4.1×10^{-3}	56
	HClO ₄	0.2	9.0×10^{-3}	56
Am(IV)	—	(4.0)	1.4×10^6	52

^a Rate constant for the formation of the peroxo-complex. ^b Estimated from a figure presented in Ref. 61. ^c Rate constant in the equation $-d[\text{Pu(III)}]/dt = k[\text{Pu(IV)}]^2[\text{H}_2\text{O}_2]$. ^d Rate constant for the formation of the peroxo-complex of Pu(IV) from the equation $d[\text{complex}]/dt = k[\text{Pu(IV)}]^2[\text{H}_2\text{O}_2]$. ^e First-order rate constant, s⁻¹. ^f Peroxide complex (decomposition).

In alkaline solutions in which the peroxide exists as HO₂⁻ and actinide anions are present, not only is the difference between the redox potentials significant but is the charge of the anion also. As the pH value increases, the rate constants, for example, for Np(VII) and Np(VI), decrease; this is due to the decrease in the difference between the potentials (the redox potentials of actinide pairs change more sharply than that of the O₂/H₂O₂ pair). However, the rate constants for Np(VII) and Np(VI) at identical pH values are close, although the potentials of the Np(VII)/Np(VI) and Np(VI)/Np(V) pairs differ by ~0.4 V. This behaviour may be due to the fact that the charge of the Np(VII)-containing anion is 3–, while that of the Np(VI) anion is 2–.

2. Reactivity of actinide ions towards ‘secondary’ inorganic and organic free radicals

In aqueous solutions, the primary radical products resulting from water radiolysis (e_{aq}⁻, H, OH, O⁻) react with dissolved compounds and are thus converted into ‘secondary’ radicals. For example, the reaction of e_{aq}⁻ with NO₃⁻ affords NO₃²⁻ radical ion, while reactions of OH with HSO₄⁻ or HCOO⁻ give rise to SO₄⁻ or CO₂⁻, respectively. In relatively concentrated solutions (more than ~0.1 mol litre⁻¹), ‘secondary’ radicals can also arise *via* the direct action of the ionising radiation on the dissolved substance. The formation of the NO₃ radical upon direct ionisation of the nitrate ion can serve as an example.

The secondary radicals possess various redox properties. Data on the redox potentials of these radicals have been reported in a number of studies.^{72–74} The potentials of the secondary radicals SO₄⁻, NO₃⁻ and Cl₂⁻ are comparable with those of the OH radical (the E° values of the latter are 1.9, 2.32 and 2.73 V in a 1 M solution of OH⁻, at pH 7 and in a 1 M solution of H⁺, respectively⁶). Therefore, the transformation of the OH radical into any other radical decreases the probability of accumulation of actinide ions in higher oxidation states during radiolysis. Note also that the introduction of certain substances in the solution makes it possible to convert the OH radical into a ‘secondary’ radical acting as a reducing agent. For example, the reaction of OH with formate ion affords the CO₂⁻ radical ion, which possesses strong reducing properties. The hydrated electron can be converted into an oxidising radical; for example, by the reaction with the peroxodisulfate ion (this reaction yields SO₄⁻). A significant radiation-induced chemical process is the reaction of e_{aq}⁻ with dinitrogen oxide; in this reaction, the OH radical (or O⁻) appears in the solution instead of the hydrated electron.

The SO₄⁻, NO₃⁻, CO₃⁻, Cl₂⁻, HO₂⁻, COOH and some other radicals also belong to the group of ‘secondary’ radicals.

a. Reactions with sulfate radicals

The SO₄⁻ radical ions are formed during radiolysis of solutions of sulfuric acid or sulfates upon the oxidation of HSO₄⁻ ions with OH radicals and upon the direct action of the ionising radiation on the sulfate ions. These radical ions can also result from irradiation of solutions containing peroxodisulfate ions.

The acid form of SO₄⁻ is the HSO₄ radical. The pK value for its dissociation is unknown. One may only believe that in neutral and probably in weakly acidic solutions, the sulfate radical exists mostly as SO₄⁻.

The rate constants for the reactions of actinide ions with sulfate radicals are listed in Table 10. It can be seen that these radicals rapidly oxidise tri- and penta-valent actinide ions and are much less reactive towards tetravalent actinide ions. The rates of reactions with U(V) and Np(III) are most likely diffusion-controlled. In the sequence Np(III)–Pu(III)–Am(III), the reactivity decreases, owing to an increase in the redox potential of the An(IV)/An(III) pair.

The main difference between the reactivities of the SO₄⁻ and OH radicals is manifested in their reactions with tetravalent actinide ions. Obviously, the oxidation of non-oxygenated ions into dioxo-ions cannot be regarded as an elementary chemical reaction. It may consist of two steps, which can formally be represented as the formation of an An⁵⁺ ion and its subsequent hydrolysis. Even in the case of U(IV), which is relatively easy to oxidise, no linear correlation exists between the measured rate constant for the pseudo-first-order reaction and the concentration of the metal ions. It cannot be ruled out that the reaction with the

Table 10. Rate constants for the reactions of actinide ions with sulfate radicals.

Actinide	Medium		$10^{-6} k$ /litre mol ⁻¹ s ⁻¹	Ref.
	I	II		
U(V)	H ₂ SO ₄	1.5	7.7×10^3	75
U(IV)	H ₂ SO ₄	2–5	$(1–8) \times 10$ (see ^a)	11
Np(V)	H ₂ SO ₄	2.0	7.0×10^2	49
Np(IV)	Solution of sulfuric acid		< 5.0	10
Np(III)	H ₂ SO ₄	3.0	3.5×10^3	76
Pu(IV)	Solution of sulfuric acid		< 5.0	10
Pu(III)	H ₂ SO ₄	5.0	5.0×10^2	77
Am(V)	MgSO ₄ + HClO ₄	1.8 + 0.2	7.0×10^2	76
Am(III)	H ₂ SO ₄ + Na ₂ S ₂ O ₈	1.0 + 1.0	2.5×10	See ^b

^a The k value depends on the concentration of U(IV); it decreases as this concentration increases. ^b Unpublished results of the authors of this review.

OH radical involves the intermediate formation of $\text{An}(\text{OH})^{4+}$, which apparently facilitates oxygenation. Perhaps this pathway is not characteristic of the sulfate radical.

b. Reactions with the NO_3 radicals

The NO_3 radicals arise in the radiolysis of acidic or neutral solutions containing nitrate ions due to the oxidation of nitric acid molecules and (to a markedly lesser extent) nitrate ions by OH radicals, or due to the direct action of ionising radiation on NO_3^- and HNO_3 (see, for example, Ref. 78).

The rate constants for the reactions of actinide ions with NO_3 radicals in aqueous solutions are presented in Table 11. The published data are limited to Np(V), Pu(III) and Am(V); however, some conclusions and predictions can also be made about the reactivity of the NO_3 radical with respect to other actinides.

Table 11. Rate constants for the reactions of actinide ions with NO_3 radicals.

Ion	Medium		$10^{-8} k$ /litre $\text{mol}^{-1} \text{s}^{-1}$	Ref.
	I	II		
Np(V)	HNO_3	1.0	8.8	49
	HNO_3	2.0	7.0	49
	HNO_3	5.0	8.4	49
	$\text{HNO}_3 + \text{LiNO}_3$	1.0 + 3.0	9.2	49
	$\text{HNO}_3 + \text{LiNO}_3$	1.0 + 6.0	6.4	49
Pu(III)	HNO_3	2.0	2.5	77
Am(V)	HNO_3	2.5	2.5	76

In the case of reactions of neptunoyl ions, the concentration of nitric acid or nitrate ions exerts no significant influence on the rate constant. A similar behaviour can be proposed for reactions of other actinoyl ions with this radical. The Pu(III) ions are oxidised relatively rapidly by the NO_3 radical. The Np(III) ions having a smaller redox potential should react with a larger rate constant. The potentials of the Am(IV)/Am(III) and $\text{NO}_3/\text{NO}_3^-$ pairs are commensurable; therefore, it may be expected that Am(III) would react with NO_3 at a low rate. The reactions of An(IV) with NO_3 occur apparently at lower rates than An(IV) + SO_4^- . The rate of the reaction between U(V) and NO_3 should be diffusion-controlled. This is attested by the fact that non-charged HSeO_3 radicals having a smaller redox potential react with U(V) at a diffusion-controlled rate: the rate constants for the U(V) + HSeO_3 reaction in 0.1 and 0.9 M solutions of HClO_4 are 1.4×10^{10} and 1.8×10^{10} litre $\text{mol}^{-1} \text{s}^{-1}$, respectively.⁷⁵

c. Reactions with molecular ions of halogens and with $(\text{CNS})_2^-$

The Cl_2^- , Br_2^- and I_2^- molecular ions derived from halogens and $(\text{CNS})_2^-$ derived from the pseudo-halogen arise during the radiolysis of aqueous solutions as a result of oxidation of halide and thiocyanate ions with OH radicals. These species are formed in several steps: first, OH adds to Hal^- (Hal^- is a halide or thiocyanate ion); the resulting HalOH^- radical ion decomposes to give Hal and OH^- , and then Hal reacts with Hal^- . In addition, these radical ions can result from oxidation of Hal^- with SO_4^- and NO_3 , from reduction of Hal_2 (for example, with e_{aq}^-) and from the direct action of ionising radiation on Hal^- .

The rate constants for the reactions of the radical ions Hal_2^- with actinide ions are listed in Table 12. The following general conclusions about the reactivity of these radical ions can be drawn.

As a rule, these radical ions are less reactive with respect to actinide ions than sulfate and nitrate radicals. This is due to the fact that the redox potentials of Hal_2^- are smaller.

Almost all the reactions involving Hal_2^- are characterised by rate constants smaller than those of the diffusion limit; in this case, it may be expected that the free energies of the reactions (or the difference ΔE° between the redox potentials of the reacting species) would have a substantial influence. The logarithms of

Table 12. Rate constants for the reactions of actinide ions with Cl_2^- , Br_2^- , I_2^- and $(\text{CNS})_2^-$ radical ions.

Actinide	Radical ion	Medium		$10^{-5} k$ (see ^a)	Ref.
		I	II		
U(V)	Cl_2^-	$\text{HCl} + \text{HClO}_4 + \text{UO}_2(\text{ClO}_4)_2$	$0.1 + 0.7 + 0.1$	4×10^4	76
	Cl_2^-	NaCl	1.0, (3)	6.5×10^3	79
	$(\text{CNS})_2^-$		(1.0)	1.46×10^4	80
U(III)	Cl_2^-	$\text{HClO}_4 + \text{HCl}$	$0.5 + 0.1$	4.8×10^4	45
	Br_2^-	$\text{HClO}_4 + \text{NaBr}$	$0.5 + 0.1$	3.4×10^4	45
	I_2^-	$\text{HClO}_4 + \text{KI}$	$0.9 + 0.1$	1.2×10^4	81, 82
	I_2^-	$\text{HClO}_4 + \text{KI}$	$0.9 + 0.1$	1.25×10^4	45
	$(\text{CNS})_2^-$	$\text{HClO}_4 + \text{NaCNS}$	$0.5 + 0.1$	1.4×10^4	45
Np(V)	Cl_2^-	HCl	1.0	3.1×10	49
	Cl_2^-	HCl	3.0	1.1×10^2	49
	Cl_2^-	$\text{HCl} + \text{LiCl}$	$0.5 + 5.0$	3.0×10^2	49
	Cl_2^-	$\text{HCl} + \text{LiClO}_4$	$0.9 + 4.0$	3.0×10^2	49
	Cl_2^-	$\text{HCl} + \text{MgCl}_2$	$0.7 + 1.5$	3.0×10^2	49
	Cl_2^-	$\text{HCl} + \text{LiCl}$	$0.8 + 3.0$	1.4×10^2	49
	Cl_2^-	NaCl	1.0, (3.0)	2.38×10^3	79
Np(III)	Br_2^-	HBr	1.0	< 10	49
	Cl_2^-	$\text{HCl} + \text{HClO}_4$	$0.1 + 0.9$	1.6×10^4	82
	Br_2^-	HBr	1.0	1.1×10^3	82
Pu(III)	I_2^-	$\text{NaI} + \text{HClO}_4$	$0.1 + 0.9$	5.0×10	82
	Cl_2^-	HCl	1.0	3.0×10^2	77
	Cl_2^-	HCl	3.0	6.0×10^2	77
Am(III)	Cl_2^-	HCl	5.0	1.2×10^3	77
	Cl_2^-	$\text{HCl} + \text{HClO}_4$	$0.01 + 5.0$	4.0×10^2	77
	Cl_2^-	$\text{HCl} + \text{H}_2\text{SO}_4$	$0.01 + 2.5$	2.3×10^2	77
	Cl_2^-	NaCl	1.0, (3.0)	4.8×10^2	79
	Br_2^-	HBr	1.0	1.6×10	77
	Cl_2^-	NaCl	1.0, (3.0)	1.5	79
	Cl_2^-	NaCl	1.0, (3.0)	3.2	79
	Cl_2^-				
	Cl_2^-				
	Cl_2^-				

^a The constants are expressed in litre $\text{mol}^{-1} \text{s}^{-1}$.

the rate constants for similar reactions of Np(III) and Pu(III) with Cl_2^- , Br_2^- and I_2^- radical ions depend linearly on ΔE° (Fig. 2).

The rates of reactions of Hal_2^- with tri- and pentavalent actinide ions are greater than those for tetravalent actinide ions [for example, according to our data, the presence of $\sim 10^{-2}$ mol/litre⁻¹ of Np(IV) or Pu(IV) has no influence on the rate of consumption of Cl_2^-], because oxidation of the latter is hampered due to the difference between the structures of the initial and oxidised ions. The mechanisms of the reactions of Hal_2^- with actinide ions include a step of formation of short-lived non-oxygenated and monooxygenated ions; the probability of transformation of these ions into final products (actinoyl ions) depends on their stability.

Oxygenated ions are also formed upon oxidation of some other ions, for example, Ti(III) and V(III). The rate constants for the reactions of Cl_2^- with the Ti(III)-, Np(III)- and Pu(III)-contain-

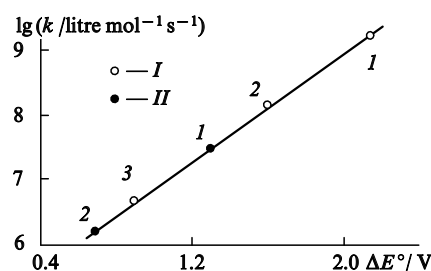


Figure 2. Dependence of the rate constants for the reactions of trivalent neptunium (I) and plutonium (II) with Cl_2^- (1), Br_2^- (2) and I_2^- (3) on the difference between the redox potentials of the reacting species.

ing aqua-ions are 1.1×10^7 , 1.0×10^9 and 3.0×10^7 litre mol⁻¹ s⁻¹, respectively, although the redox potentials for the Ti(IV)/Ti(III), Np(IV)/Np(III) and Pu(IV)/Pu(III) pairs are equal to 0.1, 0.14, and 0.97 V, respectively. The redox potential of the V(IV)/V(III) pair is 0.34 V, and the reaction of Cl₂⁻ with the V(III) aqua-ion is slower ($k < 10^6$ litre mol⁻¹ s⁻¹) than the Ti(III) + Cl₂⁻ reaction. Evidently, the oxidation of Np(III) and Pu(III) ions is not accompanied by a structural rearrangement and, therefore, it is more efficient than the oxidation of the 3*d*-element ions under consideration (even though in the case of actinide ions, valence electrons are transferred from the lower *f* orbitals).

In concentrated solutions of chlorides, inner-sphere chloro-complexes are formed; they are more reactive towards Cl₂⁻ than the corresponding aqua-ions. The logarithms of the rate constants are proportional to the concentration of chloride ions. These correlations have been obtained for the reactions of Cl₂⁻ with Np(V), Pu(III), Ce(III) and with some ions of 3*d* elements.

d. Reactions with the CO₃⁻ radical ion

The CO₃⁻ radical ions are formed during radiolysis of carbonate- and hydrogencarbonate-containing solutions. They result from reactions of the OH or O⁻ radicals with carbonate or hydrogencarbonate ions or from the direct action of ionising radiation on these ions. If the solution contains peroxodisulfate ions, CO₃⁻ can also arise *via* the reaction of SO₄⁻ with the carbonate ion. Recall that carbonates are always present as an impurity in solutions of alkali; radiolysis of these solutions can also afford CO₃⁻. The rate constants for the reactions of actinide ions with the CO₃⁻ radical ion in aqueous solutions are presented in Table 13. It should be emphasised that, depending on the concentrations of the solutes, CO₃⁻ reacts in carbonate, hydrogencarbonate and alkaline carbonate solutions with carbonate, hydroxocarbonate and hydroxo-complexes of actinides and with their oxo-anions. In these reactions, the radical ion under consideration acts as an oxidising agent.

The similarity of the electrostatic properties and structures of ions of 5*f* elements (including these ions in carbonate complexes) accounts for the linear correlations between the logarithms of rate constants and the ΔE° values of the reacting species. These correlations hold for the reactions of CO₃⁻ with the carbonate complexes of Am(III), Ce(III), Pu(III)²⁹ and U(V), Np(V), Pu(V).²¹

Table 13. Rate constants for the reactions of actinide ions with CO₃⁻ radical ions.

Actinide	Medium		10 ⁻⁵ <i>k</i> /litre mol ⁻¹ s ⁻¹	Ref.
	I	II		
U(V)	K ₂ CO ₃	0.05	4.9 × 10 ⁴	21
U(IV)	Saturated solution of KHCO ₃	—	1.4 × 10 ²	29
Np(VI)	Na ₂ CO ₃ + NaOH	0.5 + 1.0	9.0	53
Np(V)	Na ₂ CO ₃ + NaOH	0.5 + 0.2	1.8 × 10 ²	53
	Na ₂ CO ₃ + NaOH	0.5 + 0.6	2.4 × 10 ²	53
	Na ₂ CO ₃ + NaOH	0.5 + 1.0	4.4 × 10 ²	53
	Na ₂ CO ₃	0.05	1.5 × 10 ²	21
Np(IV)	Carbonate solution	—	< 5 × 10	10
Np(III)	K ₂ CO ₃	1.0	3.3 × 10 ⁴	29
	K ₂ CO ₃	3.0	1.4 × 10 ⁴	29
Pu(VI)	Na ₂ CO ₃	0.01	1.5 × 10 ²	83
Pu(V)	Na ₂ CO ₃	5 × 10 ⁻³	5.0 × 10	83
	Na ₂ CO ₃	0.05	2.7 × 10 ²	21
Pu(IV)	Carbonate solution	—	< 5 × 10	10
Pu(III)	K ₂ CO ₃	1.0	7.0 × 10 ³	29
	K ₂ CO ₃	1.1	5.6 × 10 ³	29
	K ₂ CO ₃	4.3	6.7 × 10 ³	29
	K ₂ CO ₃	3.0	2.5 × 10 ²	29
Am(III)	K ₂ CO ₃	4.6	2.7 × 10 ²	29
	K ₂ CO ₃	6.0	1.5 × 10 ²	29

The influence of the concentrations of the carbonate ions and of alkali on the reaction rate is associated with changes in the compositions of the coordination spheres of the ions and, as a consequence, in their electrostatic charges and redox potentials.

e. Reactions with the HO₂, O₂⁻ and O₃⁻ radicals

The HO₂ and O₂⁻ radicals can arise in aqueous solutions containing oxygen (mostly in reactions of oxygen with H and e_{aq}⁻). The yields of the HO₂ radicals as a primary product of radiolysis induced by heavy charged particles (including the α-particles emitted by actinides) are relatively high (see Table 2). The HO₂ and O₂⁻ radicals are in equilibrium with each other (*pK* is 4.7⁶). The O₃⁻ ion radicals are formed in an alkaline medium upon the reaction of O⁻ with oxygen. Besides, HO₂ and O₂⁻ are intermediate species formed in the reduction reactions involving hydrogen peroxide, and O₃⁻ or its acid form HO₃ [the *pK* value for the corresponding equilibrium is 6.15 (see Ref. 6)] also arise when ozone reacts with e_{aq}⁻ and H.

The rate constants for the reactions of actinide ions with HO₂, O₂⁻ and O₃⁻ radicals are listed in Table 14. Two types of reactions with actinide ions are known for HO₂ and O₂⁻, namely, electron transfer and formation of a complex. It is also noteworthy that the lifetime of O₂⁻ increases with increase in the pH, and for concentrations of alkali of more than 1 M, it reaches tens of seconds and

Table 14. Rate constants for the reactions of actinide ions with HO₂, O₂⁻ and O₃⁻ radicals.

Actinide	Medium		10 ⁻³ <i>k</i> /litre mol ⁻¹ s ⁻¹	Ref.
	I	II		
Reactions with HO ₂				
Th(IV) ^a	—	(1.0)	1.8 × 10 ³	84
Th(IV)–HO ₂	—	(1.0)	8.0 × 10 ²	84
U(VI) ^b	—	(1.0)	1.5 × 10 ²	85
U(VI)–HO ₂	—	(1.0)	9.0 × 10 ²	85
Np(V)	Acidic solution		1.1	1
Am(IV)	—	(1.0)	6.4 × 10 ⁴	52, 87
	—	(2.0)	5.2 × 10 ⁴	52, 87
	—	(3.2)	3.2 × 10 ⁴	52, 87
	—	(4.4)	2.7 × 10 ⁴	52, 87
Reactions with O ₂ ⁻				
Np(VII)	—	(8.80)	1.4 × 10 ²	64
	—	(8.97)	9.5 × 10	65
	—	(9.50)	6.5 × 10	64
	—	(9.76)	7.6 × 10	64
	—	(10.0)	5.2 × 10	64
	—	(10.7)	3.4 × 10	64
	—	(11.0)	2.6 × 10	64
	LiOH	0.1	7.2	64
	LiOH	0.2	4.7	64
	LiOH	0.5	8.8 × 10 ⁻¹	64
	LiOH	1.0	1.3	64
	Np(VI)	—	(9.18)	1.4 × 10 ²
—		(10.46)	6.5 × 10	64
—		(10.93)	5.3 × 10	64
—		(11.94)	1.45 × 10	64
LiOH		0.1	1.5	64
LiOH		0.2	6.0 × 10 ⁻²	64
LiOH		0.5	2.0 × 10 ⁻²	64
LiOH		1.0	8.0 × 10 ⁻³	64
Reactions with O ₃ ⁻				
Np(VI)	LiOH	0.2–2.0	2.1 × 10 ²	86
Np(V)	LiOH	0.2–2.0	2.0 × 10 ³	86

^a The reactions yields a complex of Th(IV) with HO₂. ^b The reaction yields a complex of U(VI) with HO₂.

^a The reactions yields a complex of Th(IV) with HO₂. ^b The reaction yields a complex of U(VI) with HO₂.

longer. Therefore, even relatively slow reactions of O_2^- with actinide ions can occur in alkaline solutions.

Attention is drawn to the fact that the reduction of Np(VI) with O_2^- radical ions occurs faster than reduction of Np(VII) under comparable conditions, although the redox potentials of the Np(VII)/Np(VI) and Np(VI)/Np(V) pairs are 0.6 and 0.15 V, respectively. In all probability, this is due to the different charges of the Np(VII)- and Np(VI)-containing ions (3- and 2-, respectively) and different structures of these ions in solution.

Reduction reactions of actinide ions with O_3^- radicals are unknown. However, decomposition of these radicals in aqueous solutions may yield hydrogen peroxide, which possesses reducing properties.

f. Reactions with organic free radicals

Organic free radicals are generated during radiolysis of aqueous solutions containing organic compounds. In concentrated solutions, they can arise from the direct action of ionising radiation on a dissolved compound.

Information on the reactivity of organic free radicals towards actinide ions is especially important for predicting the behaviour of extraction systems used in the radiochemical industry. All the organic free radicals studied exhibit reducing properties in reactions with actinide ions. The rate constants for these reactions are listed in Table 15.

It can be seen that the rates of reactions of COOH, $(CH_3)_2COH$ and electron adducts of *o*-phenanthroline, 2,2'-bipyridinium and 4,4'-dipropyl-2,2'-bipyridinium with actinide ions are high. It has been assumed that these reaction rates are limited by diffusion. Calculation of the diffusion limit rate constant for the Np(VI) + $(CH_3)_2COH$ reaction based on the Smolukhovskii equation has shown⁹¹ that the calculated and experimental values are close to each other. In addition, it was found that the activation energies for the reactions of U(VI) with the electron adducts of *o*-phenanthroline and 2,2'-bipyridinium are 10 and 16.7 kJ mol⁻¹, respectively. These magnitudes are typical of reactions the rates of which are diffusion-controlled or are close to the diffusion limit.

Uranium, neptunium, plutonium and americium ions react with the H adducts of *o*-phenanthroline and 2,2'-bipyridinium much more slowly than with the corresponding electron adducts. This is due most likely to the difference between the structures of the electron and H adducts. Thus it has been suggested⁹² that the electron adduct of *o*-phenanthroline is protonated at the second nitrogen atom in the molecule, whereas in the case of the H adduct, the additional hydrogen atom adds to one of the ring carbon atoms. Therefore, the excess electron in the electron adducts is delocalised over the aromatic π -system, whereas in H adducts, this system is broken to give a cyclodienyl type radical. In the former case, the transfer of an electron occurs readily, while in the latter case it is hampered.

It should be emphasised that the reactivity of actinide ions towards organic free radicals has been markedly less studied than their reactivity with respect to inorganic radicals. This is especially true for the organic radicals that are formed upon radiolysis of extraction systems used for practical purposes. Certainly, more extensive studies in this field would be expedient.

Thus, the following general conclusions can be drawn about the reactivity of actinide ions towards inorganic and organic free radicals in aqueous solutions (see also Refs 1, 11–13).

(1) If the ΔE° value of the species involved in reactions occurring by the mechanism of outer-sphere electron transfer is relatively large (~ 2.3 V and larger), the rates of these reactions are diffusion-controlled or are close to the diffusion limit. However, if the reaction occurs by a complicated mechanism including, for example, complex formation or a structural rearrangement of the actinide ion, this conclusion may be false.

(2) When the reaction rate is not diffusion-controlled, it often depends on the redox potentials of the actinide ions and the radicals participating in the reaction. For example, the reactivity

Table 15. Rate constants for the reactions of actinides with organic free radicals.

Actinide	Radical	Medium		$10^{-7} k$ (see ^a)	Ref.
		I	II		
U(VI)	COOH	H ₂ SO ₄ + HCOOH	1.0 + 5.3	1.0×10^2	88
	COOH	H ₂ SO ₄ + HCOOH	0.4 + 5.3	7.3×10	88
	COOH	H ₂ SO ₄ + HCOOH	0.048 + 5.3	1.0×10^2	88
	COOH	HCOOH	5.3	1.6×10^2	88
	COOH	HCOOH	12.2	1.5×10^2	88
	COOH	HCOOH	17.7	1.3×10^2	88
	COOH	HCOOH	24.4	3.4×10^2	88
	COOH	HCOOH	26.2	5.9×10^2	88
	$(CH_3)_2COH$	H ₂ SO ₄	0.1	2.4×10^2	13
	$(CH_3)_2COH$	—	(~ 1.0)	4.7	59
	BpyH ₂ ⁺ (see ^b)	HClO ₄	0.1	9.0	13
	BpyH ₂ ⁺	H ₂ SO ₄ + HCOOH	1.0 + 5.3	1.1×10	88
	BpyH ₂ ⁺	H ₂ SO ₄ + HCOOH	0.4 + 5.3	8.6	88
	BpyH ₂ ⁺	H ₂ SO ₄ + HCOOH	0.048 + 5.3	7.0	88
	BpyH ₂ ⁺	HCOOH	5.3	6.6	88
	BpyH ₂ ⁺	HCOOH	12.2	6.0	88
	BpyH ₂ ⁺	HCOOH	24.4	1.0×10	88
	PhenH ₂ ⁺ (see ^c)	HCOOH	5.3	9.1	88
	PhenH ₂ ⁺	H ₂ SO ₄ + HCOOH	0.4 + 5.3	1.0×10	88
	PhenH ₂ ⁺	HCOOH	17.7	8.4	88
	PhenH ₂ ⁺	HCOOH	26.2	1.0×10	88
	H.PhenH ⁺ (see ^d)	HClO ₄	0.1	$< 2.0 \times 10^{-1}$	89
	R (see ^e)	—	(4.0)	9.8	90
U(III)	CH ₃ (see ^f)	HClO ₄	0.5	1.5×10^2	45
	CH ₂ OH	HClO ₄	0.5	< 2.0	45
	CH ₂ COOH	HClO ₄	0.5	1.2×10	45
	(see ^f)				
	$(CH_3)_2COH$	HClO ₄	0.5	< 1.0	45
	CH ₃ CHCOOH	HClO ₄	0.5	2.1	45
	(see ^f)				
	CH ₂ C(CH ₃) ₂ OH	HClO ₄	0.5	$< 5.0 \times 10^{-1}$	45
Np(VI)	COOH	HCOOH	12.2	8.7×10^3	88
	COOH	HCOOH	24.4	9.0×10^3	88
	$(CH_3)_2COH$	HClO ₄	0.1	1.8×10^3	91
	BpyH ₂ ⁺	HClO ₄	0.1	8.0×10	91
	BpyH ₂ ⁺	H ₂ SO ₄ + + HCOOH	0.1 + 2.6	1.9×10^2	88
	BpyH ₂ ⁺	HCOOH	12.2	1.9×10^2	88
	BpyH ₂ ⁺	HCOOH	24.4	1.5×10^2	88
	PhenH ₂ ⁺	HClO ₄	0.1	5.0×10	91
	H.PhenH ⁺	H ₂ SO ₄	0.1	$\leq 3.5 \times 10^{-1}$	91
	R	—	(4.0)	2.27×10^2	90
	(CH ₃) ₂ COH	HClO ₄	0.1	1.6×10^3	91
	BpyH ₂ ⁺	HClO ₄	0.1	1.5×10^2	91
Pu(VI)	PhenH ₂ ⁺	HClO ₄	0.1	1.3×10^2	91
	R	—	(4.0)	2.26×10^2	90

^a Expressed in litre mol⁻¹ s⁻¹. ^b From here on, this is the electron adduct of 2,2'-bipyridinium. ^c From here on, this is the electron adduct of *o*-phenanthroline. ^d From here on, this is the H-adduct of *o*-phenanthroline. ^e From here on, R is the electron adduct of 4,4'-dipropyl-2,2'-bipyridinium. ^f The reaction yields the product of addition of the radical to U(III).

of radicals in oxidation processes changes in the following sequence: $SO_4^- > NO_3^- > OH^- > Cl_2^- > Br_2^- > I_2^- > O_3^-$.

(3) If the structures of actinide ions and free radicals reacting with them are similar, for analogous reactions the rates of which are not diffusion-controlled, the logarithms of rate constants obey a linear correlation with the ΔE° values of the reacting species (see Figs 1 and 2).

(4) The reactivity of actinide ions is markedly influenced by the formation of complexes. It was noted above that the rate constants for reactions of Np(III) and Pu(III) with the Cl_2^- radical ion increase following an increase in the concentration of chloride ions in the solution. This is due to the formation of inner-sphere chloride complexes possessing a higher reactivity towards Cl_2^- (it has been found that an increase in the concentrations of HClO_4 , LiClO_4 or H_2SO_4 barely influences the rates of the corresponding reactions).

(5) A structural change in the coordination sphere of an actinide ion upon reaction is among the factors having an influence on the reaction rate. For example, this is true for oxidation of An(IV) or reduction of An(V). In these processes, non-oxygenated multi-charged cations are converted into oxygenated cations and *vice versa*. The reactivity can depend on the stability of intermediate ions.

(6) If the rate of the reaction of an actinide ion with a radical ion is not diffusion-controlled, the rate constant depends on the charge of the actinide-containing ion. Among other factors, this may be due to hydrolysis of actinide ions. In some cases, the magnitude of this effect surpasses the influence of the redox potential. This is observed in the reactions of O_2^- with Np(VI) and Np(VII) ions in alkaline media.

IV. Uranium

Radiolytic transformations of uranium ions in aqueous solutions induced by γ - and α -radiation have been studied fairly comprehensively. The main results obtained in these studies are outlined below and are interpreted resorting to the published data on the kinetics of reactions of uranium ions with the products of radiolysis of water and with 'secondary' free radicals.

1. γ -Radiolysis of acidic aqueous solutions of uranium ions

The behaviour of uranium ions in aqueous solutions under the action of X-rays and γ -radiation has been studied; this includes reduction of U(VI) in the presence of acceptors of OH radicals and in the absence of oxygen as well as oxidation of U(III) and U(IV) in deaerated solutions and oxidation of U(IV) in solutions saturated with air.

It is known¹ that when aerated solutions of U(VI) (> 0.2 mol litre⁻¹) in 0.05 M H_2SO_4 are exposed to γ -radiation, the concentration of U(VI) ions does not change and no hydrogen peroxide is detected. This can be explained in the following way: U(VI) is reduced in reactions with e_{aq}^- and H (H is formed not only as a product of water radiolysis but also in the reaction of e_{aq}^- with H^+) to U(V); however, the latter is again oxidised to U(VI) in reactions with OH and H radicals and also with hydrogen peroxide. In neutral and weakly acidic solutions, peroxide complexes of U(VI) are formed; after relatively prolonged irradiation, they precipitate. In sufficiently acidic media, these complexes are soluble, and no precipitate is formed. In solutions saturated with air, U(VI) ions form a complex with the HO_2 radical; disproportionation of this complex yields U(VI) and hydrogen peroxide.

Reduction of U(VI) occurs in solutions containing organic compounds (Table 16).^{93, 94} In these systems, reactions of H and OH with organic compounds (we denote them by RH_2) are significant. These reactions afford 'RH' radicals able to reduce U(VI). The U(V) ions resulting from reduction of U(VI) disproportionate to give U(IV) and U(VI). Note that the intermediate formation of U(V) in the radiolytic reduction of U(VI) and oxidation of U(IV) has been confirmed electrochemically.¹

The formation of one U(IV) ion requires two reducing radicals or two OH radicals. Hydrogen peroxide oxidises U(IV) to U(V) or oxidises U(V) to U(VI), and the OH radical thus formed reacts with RH_2 . Therefore, the theoretical reduction yield of U(VI) attained in the case where all the OH radicals are trapped by an organic compound should be $(G_{e_{\text{aq}}^-} + G_{\text{H}} + G_{\text{OH}})/2 = 3.3$ ion (100 eV)⁻¹. [This is valid, provided that 'RH reduces U(VI)']. In the presence of *tert*-butyl alcohol, no reduction by an organic radical occurs, because the free radical resulting from the reaction of *tert*-butyl alcohol with OH and H radicals is not a reducing agent (see

Table 16. Reduction yields of U(VI) in γ -radiolysis of deaerated solutions of U(VI) containing organic compounds RH_2 .^{93, 94}

RH_2	$[\text{RH}_2]$ /M	$G[-(\text{U(VI)})]$ (see ^a)	RH_2	$[\text{RH}_2]$ /M	$G[-(\text{U(VI)})]$ (see ^a)
CH_3OH	0.1	2.6	$(\text{CH}_3)_3\text{COH}$	0.2	1.0
CH_3OH	0.5	3.0	$(\text{CH}_3)_3\text{COH}$	0.5	1.1
CH_3OH	1.0	3.0	$(\text{CH}_3)_3\text{COH}$	0.75	1.3
$\text{C}_2\text{H}_5\text{OH}$	0.5	3.2	$(\text{CH}_3)_3\text{COH}$	1.0	1.3
$(\text{CH}_3)_2\text{CHOH}$	0.5	3.6	HCOOH	0.1	2.3
$(\text{CH}_3)_3\text{COH}$	0.01	0.7	$\text{H}_2\text{C}_2\text{O}_4$ (see ^b)	0.005	0
$(\text{CH}_3)_3\text{COH}$	0.05	0.8	$\text{H}_2\text{C}_2\text{O}_4$ (see ^b)	0.01	0.3
$(\text{CH}_3)_3\text{COH}$	0.1	0.9	$\text{H}_2\text{C}_2\text{O}_4$ (see ^b)	0.1	2.3
			$\text{H}_2\text{C}_2\text{O}_4$ (see ^b)	0.3	2.7

^a Expressed in ion (100 eV)⁻¹. ^b Estimated from a figure presented in Ref. 93.

Table 16). Since in this system hydrated electrons not only reduce U(VI) but also react with H^+ to give H atoms and the latter can partly react with *tert*-butyl alcohol, the reduction yield attained can be found from the following expression:

$$G[-\text{U(VI)}] = G[\text{U(IV)}] < \frac{1}{2}(G_{e_{\text{aq}}^-} + G_{\text{H}} - G_{\text{H}_2\text{O}_2}), \quad (3)$$

i.e. $G[-\text{U(VI)}]$ should be smaller than 1.4 ion (100 eV)⁻¹.

It has been shown⁹³ that the reduction yield of U(VI) in solutions containing $\text{H}_2\text{C}_2\text{O}_4$ decreases when sulfuric acid is added. This can be explained by the fact that HC_2O_4^- , $\text{H}_2\text{C}_2\text{O}_4$ and HSO_4^- compete for OH radicals (the rate constants for the corresponding reactions are commensurable⁹⁵). The two species mentioned first react to give reducing radicals, whereas the reaction with HSO_4^- affords an oxidising radical, which, like the OH radical, is able to oxidise U(IV) and U(V).

When the concentration of organic substances is high, recombination of OH radicals in spurs is partially suppressed, and the reduction yield of U(VI) thus increases.⁹⁴

Reduction of U(VI) also occurs⁹⁶ in solutions of nitric acid containing sulfanilamide. The latter reacts with nitrous acid and with NO_3 radicals formed in this system, and this precludes the reverse oxidation of U(V) and U(IV). The reduction yield of U(VI) amounts to 1.3 ion (100 eV)⁻¹.

Radiolytic processes in aqueous solutions of U(IV) have also been the objects of several experimental and computer studies.⁹⁷ In deaerated solutions of U(IV) in perchloric acid, U(IV) is oxidised to U(VI).¹ The oxidation yield increases as the concentration of U(IV) increases; for $[\text{U(IV)}] = 0.05$ mol litre⁻¹ in 0.1 M HClO_4 , it is 2.45 ion (100 eV)⁻¹. At higher concentrations of U(IV), the yield is somewhat lower. In some cases, both $G[-\text{U(IV)}]$ and $G(\text{H}_2)$ have been measured. It was found that $G(\text{H}_2)$ is much larger than G_{H_2} . The most significant processes in this system are oxidation of U(IV) with OH radicals and with hydrogen peroxide, oxidation of U(V) with H atoms, disproportionation of U(V), reduction of U(IV), U(V) and U(VI) with hydrated electrons and the interaction of U(III) with U(V) and U(VI). With allowance for all these reactions and for the data of Table 1, the $G[-\text{U(IV)}]$ value, which is equal to $G[\text{U(VI)}]$, is 2.3 ion (100 eV)⁻¹.

It has been noted⁴⁴ that oxidation of U(III) [resulting from the reduction of U(IV) with H atoms] may be ignored in the mechanism of the oxidation of U(IV), because U(III) reacts rapidly with U(V) and U(VI), the concentrations of which are much higher than the steady-state concentration of H atoms. The U(V) ions are long-lived species; therefore their concentration during γ -radiolysis is relatively high.

Vladimirova⁹⁷ carried out computer modelling of the radiolysis of deaerated solutions of U(IV) in perchloric acid. Unfortunately, the researcher assumed without proof that the reaction of U(VI) with HO_2 yields U(IV) rather than a complex of U(VI) with HO_2 .

When deaerated solutions of U(IV) in aqueous sulfuric acid are exposed to γ -radiation, as in the case of solutions in perchloric acid, U(IV) is oxidised.¹ In a 0.4 M solution of sulfuric acid, the $G[-\text{U(IV)}]$ value increases following an increase in the concen-

tration of U(IV) and is $2.0\text{--}2.4\text{ ion (100 eV)}^{-1}$ in the range of its concentrations of $0.02\text{--}0.05\text{ mol litre}^{-1}$. Upon further increase in the concentration of U(IV), the yield decreases; in a $0.5\text{ mol litre}^{-1}$ solution, $G[-\text{U(IV)}]$ is $\sim 0.8\text{ ion (100 eV)}^{-1}$. Evidently, the mechanisms of the radiolysis of solutions containing sulfuric and perchloric acids are similar. In all probability, the decrease in $G[-\text{U(IV)}]$ at high concentrations of U(IV) is due to the fact that some of the uranium ions trap the reducing radicals from spurs. Study of radiolytic oxidation of U(IV) has shown that at elevated temperatures, H atoms are also involved in the oxidation, in addition to OH and H_2O_2 ; therefore, in this case, the oxidation yield is higher than that at room temperature.

γ -Radiolysis of deaerated aqueous solutions of U(IV) in hydrochloric acid has been studied in a number of publications.^{1, 57} It was found that the oxidation yield decreases upon an increase in the concentration of HCl and increases following an increase in the concentration of U(IV); however, $G[-\text{U(IV)}]$ is much lower than that in solutions containing sulfuric acid.

Oxidation of U(IV) induced by γ -radiation or X-rays in air-saturated solutions in sulfuric acid has been the object of several studies.¹ It was noted that the radiolytic oxidation of U(IV) ions in this system is complicated by their spontaneous oxidation with the atmospheric oxygen. The initial oxidation yields slowly increase when the concentration of U(IV) increases and decrease as the dose rate increases.

Radiolytic oxidation of U(IV) in $0.5\text{--}3\text{ M HNO}_3$ saturated with air has been studied.⁹⁸ To bind nitrous acid which is able to oxidise U(IV), hydrazine (up to $0.1\text{ mol litre}^{-1}$) was added to the solutions. The oxidation yields were found to decrease with an increase in the concentration of nitric acid. In the presence of U(VI), the yields decrease somewhat. In this system, U(IV) is oxidised by the NO_3 radical (arising in the reaction of OH radicals with nitric acid and NO_3^-), by molecular oxygen and by hydrogen peroxide. The U(VI) introduced into the solution is reduced by intermediate compounds formed in the oxidation of hydrazine; therefore, the oxidation yield of U(IV) diminishes.

A scheme consisting of twenty reactions has been proposed for the mathematical description of radiolytic oxidation of U(IV) in solutions containing nitric acid.⁹⁹ The results obtained in terms of this scheme, after selection of unknown rate constants, were apparently in satisfactory agreement with the experimental data.

The oxidation yields of U(IV) during radiolysis of hydrochloric-acid solutions (with a dose rate of 0.39 Gy s^{-1}) saturated with air are lower than those in aerated solutions of sulfuric acid.¹ For example, the maximum yield in air-saturated 0.8 M HCl amounts to $7.8\text{ ion (100 eV)}^{-1}$.⁵⁷

Trivalent uranium is oxidised during radiolysis in aqueous solutions to give U(IV).¹ Thus its oxidation yield in hydrochloric acid reaches $\sim 12\text{ ion (100 eV)}^{-1}$. If we assume that U(III) is oxidised *via* interaction with H, OH, Cl_2^- and H_2O_2 , the calculated oxidation yield is $8.2\text{ ion (100 eV)}^{-1}$. The experimental value is markedly higher. Perhaps, the solutions were not completely free from oxygen during irradiation.

2. α -Radiolysis of acidic aqueous solutions of uranium ions

Most of the studies dealt with the oxidation of U(IV) in deaerated and aerated aqueous solutions of various acids during α -radiolysis. It has been noted¹ that when solutions of U(VI) in sulfuric acid are exposed to α -particles emitted by radon, uranium is not reduced. When a solution containing both U(IV) and U(VI) has been irradiated by α -particles from radon, U(IV) has been oxidised. In a study of α -radiolysis of deaerated solutions of U(IV) in sulfuric acid, it has been found that the oxidation yield of U(IV) and the yield of formation of molecular hydrogen diminish following an increase in the concentration of U(IV). Uranium(IV) is oxidised by hydrogen peroxide, OH and HO_2 radicals, whereas H atoms (in this medium, they appear instead of hydrated electrons) reduce the resulting U(VI). Thus

$$G[-\text{U(IV)}] = \frac{1}{2}G_{\text{OH}} + G_{\text{H}_2\text{O}_2} + \frac{3}{2} - G_{\text{HO}_2} - [G_{\text{H}_2} - G(\text{H}_2)] - \frac{1}{2}(G_{e_{\text{aq}}^-} + G_{\text{H}}). \quad (4)$$

For example, the $G[-\text{U(IV)}]$ value calculated for a $2 \times 10^{-3}\text{ mol litre}^{-1}$ solution of U(IV) in $1.5\text{ M H}_2\text{SO}_4$ using the primary yields of the products of α -radiolysis of water given in Table 2 is $1.19\text{ ion (100 eV)}^{-1}$. This value differs somewhat from that found experimentally [$1.08\text{ ion (100 eV)}^{-1}$]. This difference can be due to the fact that the primary yields refer to a 0.4 M solution of sulfuric acid, while the experimental value was measured for $1.5\text{ M H}_2\text{SO}_4$.

The oxidation yield of U(IV) in aerated acidic solutions is markedly higher; it increases with an increase in the concentration of U(IV) and with a decrease in the dose rate.¹ The reactions occurring during α -radiolysis of solutions saturated with air are the same as those occurring during γ -radiolysis. The facts that the oxidation yields induced by α - and γ -radiolyses are high and that they depend on the radiation dose rate indicate that the oxidation of U(IV) follows a chain mechanism.

Study of the influence of the energy of helions (*i.e.* linear transfer of energy) on the $G[\text{U(VI)}]$ values for the oxidation of U(IV) in 0.4 M solutions of H_2SO_4 saturated with oxygen or nitrogen has shown that the oxidation yields in oxygen-saturated solutions increase with an increase in the energy of helions, whereas for solutions saturated with nitrogen, the opposite dependence is observed.¹⁰⁰

Oxidation of U(IV) in $0.2\text{--}11.5\text{ M}$ solutions of HClO_4 exposed to intense α -radiation from ^{244}Cm has been studied.¹⁰¹ Curium was added to the solution as a solid salt or as its solution. In the former case, the oxidation yield was equal to $1.6\text{ ion (100 eV)}^{-1}$ in $0.2\text{--}1\text{ M}$ solutions of HClO_4 and increased gradually following an increase in the concentration of the acid; in $10\text{--}11\text{ M HClO}_4$ the oxidation yield was equal to $\sim 6\text{ ion (100 eV)}^{-1}$ $\{[\text{U(IV)}] = 6.6 \times 10^{-3}\text{ mol litre}^{-1}\}$. It was shown that the yield is almost independent of the dose rate but increases with an increase in the concentration of U(IV). When curium was introduced as a solution, the oxidation yields were $2.7, 7.5$ and $50\text{ ion (100 eV)}^{-1}$ for concentrations of HClO_4 of $0.2, 4$ and 7 M , respectively. Evidently, the latter value was markedly overestimated. Oxidation of U(IV) occurs *via* the same reactions as it does in solutions containing sulfuric acid. The higher yields attained in this case can be due to the influence of the products of decomposition of HClO_4 ($\text{ClO}_2, \text{Cl}_2, \text{ClO}_2^-$) formed during radiolysis.

It was found¹⁰¹ that the oxidation yield of U(IV) in nitric-acid solutions during radiolysis induced by α -particles from ^{244}Cm decreases as the content of HNO_3 increases. For concentrations of the acid of $0.5\text{--}1$ and $2\text{--}8\text{ M}$, the yields are ~ 2 and $\sim 1\text{ ion (100 eV)}^{-1}$, respectively. When the concentration of HNO_3 is further increased, the yield drops almost to zero. The yields in solutions containing nitric acid are lower than those in solutions of sulfuric and perchloric acids. This is due to the formation of HNO_2 , which reacts with H_2O_2 and, possibly, with HO_2 .

V. Neptunium

Vast information dealing with radiolytic transformations of neptunium ions in acidic, carbonate-containing and alkaline solutions exposed to γ - and α -radiation can be found in the literature.

1. γ -Radiolysis of acidic aqueous solutions of neptunium ions

γ -Radiolysis of aerated solutions of Np(VI) containing perchloric acid results in accumulation of Np(V); $G[-\text{Np(VI)}] = G[\text{Np(V)}] = 2.4\text{ ion (100 eV)}^{-1}$.¹⁰² The mechanism of this process in a weakly acidic solution includes reactions of Np(VI) with e_{aq}^- , H, HO_2 and H_2O_2 as well as reverse oxidation of Np(V) with OH radicals; the calculated value of $G[-\text{Np(VI)}]$ {or $G[\text{Np(V)}]$ } is $2.3\text{ ion (100 eV)}^{-1}$. The yield measured in another study¹⁰² coincides with this value. However, earlier publications (they have been considered in a previous monograph¹) report values

of 4.0 to 6.7 ion (100 eV)⁻¹, depending on the concentrations of Np(VI) and HClO₄. Among other reasons, such high yields may be due to the presence of organic impurities in the solutions used. In a 3.4 M solution of HClO₄, $G[-\text{Np(VI)}]$ was found to be 1.9 ion (100 eV)⁻¹. This low yield can be due to the fact that the reduction of Np(VI) with hydrogen peroxide and HO₂ radicals is retarded and also due to the fact that HO₂ participates to some extent in the oxidation of the resulting Np(V).

The radiolytic behaviour of Np(V) in aerated solutions in perchloric acid has been studied in detail.¹⁰² It was found that Np(V) is fairly stable in these solutions. In particular, in 1 M HClO₄, the formation of Np(VI) has been observed only at relatively high radiation doses. In the presence of acceptors that transform hydrated electrons and H atoms into OH radicals, Np(V) is oxidised irreversibly into Np(VI) under the action of γ -irradiation.¹⁰² In solutions with pH $\geq$ 4, dinitrogen oxide was used as the acceptor. The initial oxidation yield $G[-\text{Np(V)}]$, which is equal to $G[\text{Np(VI)}]$, was 2.1 ion (100 eV)⁻¹. At pH $\leq$ 1, xenon trioxide served as the acceptor; it reacted with H to give XeO₂ and OH. It should be noted that in this system, HO₂ radicals and, finally, hydrogen peroxide are also converted into OH radicals. The oxidation yield depends on the concentration of XeO₃; it increases from 6 for 1×10^{-3} mol litre⁻¹ of XeO₃ to 13.5 ion (100 eV)⁻¹ for 2×10^{-2} mol litre⁻¹ of XeO₃. The mechanism of the radiolytic oxidation of Np(V) in the presence of the acceptors mentioned above has been discussed in Ref. 1.

Radiolytic reduction of Np(VI) and oxidation of Np(IV) in solutions containing sulfuric acid have been studied. Reduction of Np(VI) in these solutions has been described in a number of publications (they are discussed in Ref. 1). The reduction yields range from 4.5–5.0 ion (100 eV)⁻¹ in $\sim 10^{-3}$ – 10^{-2} M solutions of H₂SO₄ to 2.5–3.0 ion (100 eV)⁻¹ in ~ 0.4 – 0.5 M solutions of this acid.

The mechanisms of reduction of Np(VI) in solutions of sulfuric and perchloric acids are similar. The calculated reduction yield in these solutions is 2.3 ion (100 eV)⁻¹. The experimental $G[-\text{Np(VI)}]$ values for solutions in sulfuric acid are higher, which is apparently due to the presence of organic impurities.¹

Reduction of Np(VI) with the heteropoly-blue PW₁₂O₄₀⁴⁻ in a 0.1 M solution of H₂SO₄ has been studied by pulse radiolysis.¹⁰³ The rate constant of the corresponding reaction was measured to be 3.2×10^8 litre mol⁻¹ s⁻¹. This is smaller than the diffusion limit rate constants for reactions of oppositely charged ions. The kinetic restrictions during electron transfer are apparently due to the fact that the excess electron is delocalised over the tungsten atoms shielded by the negatively charged oxygen atoms.¹⁰⁴

Radiolytic oxidation of Np(IV) to Np(V) in aqueous solutions of sulfuric acid has been studied by several researchers (these studies have been surveyed in Ref. 1). In particular, it was found that in aerated solutions the yield increases from ~ 13 to 15 ion (100 eV)⁻¹ on passing from 1×10^{-2} M to 0.4 M H₂SO₄. Oxidation of Np(IV) in aerated solutions is accomplished *via* reactions with HO₂ (this radical results from interaction of H with O₂), OH and H₂O₂. Therefore, the theoretical value of $G[-\text{Np(IV)}]$ is 15.5 ion (100 eV)⁻¹ for 0.4–0.5 M H₂SO₄. This value differs only slightly from the experimental result.

Data on radiolytic processes including reduction of Np(VI) and oxidation of Np(IV) in nitric acid solutions have been reported.

When solutions of Np(VI) in 1×10^{-3} – 2 M HNO₃ are exposed to high-energy electrons or to γ -radiation, Np(V) ions are formed.^{1,4} The reduction yields decrease with an increase in the concentration of nitric acid or in the dose rate. A peculiar feature of the radiolysis of these solutions is the existence of an induction period at high concentrations of HNO₃.

During γ -radiolysis of aerated solutions of Np(VI) in nitric acid, the following intermediate species are formed: NO₃²⁻ (resulting from the reaction of e_{aq}⁻ with NO₃⁻), HNO₃⁻ (the reaction of H with NO₃⁻) and NO₃ (the reactions of OH with HNO₃ and NO₃⁻ and direct action of ionising radiation on the nitrate ion). When the concentration of NO₃⁻ is low, the reaction between H and O₂ is also possible. The OH radical can participate in the oxidation of

the Np(V) formed, but at low radiation doses, this process can be neglected. In an acidic medium, the NO₃²⁻ and HNO₃⁻ radical ions are converted into NO₂; the latter reacts with water to give HNO₂ and NO₃⁻. In concentrated solutions of nitric acid, NO₂ and NO₃ radicals can also arise from the direct action of the ionising radiation on HNO₃ and NO₃⁻.⁶

The NO₃ radicals oxidise Np(V) and undergo dimerisation or hydrolysis. Hydrolysis yields NO₂ and hydrogen peroxide. The dimer N₂O₆ can reduce Np(VI).¹ The dimerisation of NO₃ radicals is fairly significant in concentrated solutions of HNO₃ in which these radicals are formed in a high yield upon interaction of NO₃⁻ and HNO₃ with OH and also upon direct action of the ionising radiation on the solute. In addition, trapping of reducing radicals by nitrate ions in spurs should also be taken into account. Nitrous acid reduces Np(VI) and destroys hydrogen peroxide. As the concentration of H⁺ increases, the rate of the reaction of this acid with Np(VI) decreases, while the rate of the reaction with hydrogen peroxide increases.

Reduction of Np(VI) in aerated 1×10^{-3} – 5×10^{-2} M solutions of HNO₃ occurs *via* its reactions with the HO₂ radical, hydrogen peroxide and nitrous acid. The reaction between HNO₂ and H₂O₂ in these solutions can be ignored. The resulting Np(V) is oxidised by the NO₃ and OH radicals. When the concentration of HNO₃ is 1 M or higher, the mechanism of radiolytic transformations becomes somewhat different. Firstly, hydrogen atoms are consumed in the reactions with NO₃⁻, whereas the reaction between H and O₂ plays only a minor role; secondly, the rates of reactions of Np(VI) with HO₂ and HNO₂ decrease; thirdly, the reaction between HNO₂ and H₂O₂ accelerates; fourthly, Np(V) is reduced by nitrous acid. A decrease in the dose rate results in a decrease in the concentrations of H₂O₂ and HNO₂; hence, the rate of the reaction between these species decreases, and the proportions of H₂O₂ and HNO₂ that react with Np(VI) increase.

The existence of an 'induction period' in concentrated solutions of HNO₃ can be explained by the fact that the reaction between Np(VI) and hydrogen peroxide in these systems occurs slowly, and Np(V) appears only after accumulation of a fairly large amount of HNO₂ in the solution.

The influence of U(VI) on the radiolytic reduction of Np(VI) in solutions of nitric acid has been studied.¹ An increase in the concentration of U(VI) leads to an increase in the yield of Np(V). It was postulated that a cation–cation complex formed by U(VI) and Np(V) plays an important role in this process. However, later it has been shown¹⁰⁵ that the radiolytic transformations in this system can be interpreted without invoking the idea of cation–cation interactions. It was noted¹ that the introduction of Ce(IV) (up to $\sim 2 \times 10^{-2}$ mol litre⁻¹) exerts no influence on the yield of Np(V).

On exposure to γ -radiation, Np(IV) ions in aerated and deaerated solutions of nitric acid are oxidised to Np(V) (for concentrations of HNO₃ ranging from 1×10^{-3} to 0.5 M) and to Np(VI).^{1,106} The oxidation yield of Np(IV) in aerated solutions depends on the concentration of nitric acid: initially, it increases from 7 to 9 ion (100 eV)⁻¹ following an increase in the [HNO₃] value from 5×10^{-3} to 0.1 M, and then it decreases to 1.5 to 2.6 ion (100 eV)⁻¹ for [HNO₃] = 1–6 M. In the case of deaerated solutions, this yield is almost constant, 4.0 to 4.6 ion (100 eV)⁻¹ ([HNO₃] = 5×10^{-3} – 0.4 M).^{1,106}

During γ -radiolysis of deaerated solutions, NO₂, NO₃ and HNO₂ are formed; Np(IV) reacts with OH, HO₂, H₂O₂ and e_{aq}⁻, and Np(III) reacts with Np(V). The role of the reaction between HNO₂ and H₂O₂ is relatively small. The formation of NO₃ under the action of ionising radiation can be neglected at [HNO₃] $\leq$ 0.4 M. It is assumed that HNO₂ does not react with Np(IV). For concentrations of HNO₃ equal to 0.1 and 0.4 M, the reaction of Np(IV) with e_{aq}⁻ and, hence, the reaction between Np(III) and Np(V) can be ignored. For these solutions

$$G[-\text{Np(IV)}] = G_{\text{OH}} + 2G_{\text{H}_2\text{O}_2} = 4.55 \text{ ion (100 eV)}^{-1}.$$

The experimental $G[-\text{Np(IV)}]$ values found for the above concentrations of HNO₃ are close to this value. The fact that at

low concentrations of HNO_3 , the $G[-\text{Np(IV)}]$ values are smaller is due to the occurrence of the reactions between Np(IV) and e_{aq}^- and between Np(III) and Np(V) .

In 5×10^{-3} – 0.5 M solutions of HNO_3 saturated with air, the oxidation yield of Np(IV) should be higher than that in deaerated solutions, since the former contain HO_2 radicals (resulting from the reaction of H with O_2) able to oxidise Np(IV) . In aerated 1 to 6 M solutions of HNO_3 , the reaction with HO_2 is insignificant, H_2O_2 reacts completely with HNO_2 , and the OH radicals are consumed to give NO_3 . The yield of NO_3 is larger than G_{OH} owing to the direct action of the ionising radiation on NO_3^- and HNO_3 . However, $G[-\text{Np(IV)}] < G_{\text{OH}}$. This is apparently due to the fact that not all the NO_3 radicals are consumed in the reaction with Np(IV) ; some of these radicals can be hydrolysed and involved in the oxidation of nitrous acid. A decrease in the concentration of Np(IV) is favourable for the side reactions of NO_3 .

According to Rotmanov *et al.*,¹⁰⁷ prolonged irradiation of solutions of tetravalent neptunium in aqueous nitric acid results in the establishment of steady-state (equilibrium, as the researchers state) concentrations of HNO_2 , Np(IV) , Np(V) and Np(VI) . For example, when the initial concentrations of Np(IV) and HNO_3 are 3×10^{-3} and 1 mol litre^{-1} , the steady-state concentrations are the following: $7.5 \times 10^{-5} \text{ mol litre}^{-1}$ (HNO_2) and 3%, 92% and 5% [Np(IV) , Np(V) and Np(VI) , respectively]. In the case where the concentrations of Np(IV) and HNO_3 are 3×10^{-3} and 6 mol litre^{-1} , the steady-state concentrations are equal to $1.6 \times 10^{-4} \text{ mol litre}^{-1}$ and 36%, 40% and 24%, respectively. It can be seen that as the concentration of nitric acid increases, the steady-state concentrations of Np(IV) and Np(VI) increase. This is due to the reaction between Np(VI) and HNO_2 and to disproportionation of Np(V) .

2. α -Radiolysis of acidic aqueous solutions of neptunium ions

α -Radiolysis of tetravalent and hexavalent neptunium has been studied in solutions containing perchloric and nitric acids. Under the action of its own α -radiation, Np(VI) ions in 0.48 – 1.7 M solutions of HClO_4 are converted into Np(V) .¹ The rate constant for the reduction in 0.044 – 0.3 M solutions of Np(VI) is $3.1 \times 10^{-9} \text{ s}^{-1}$. Using this value, the half-life period of ^{237}Np (2.2×10^6 years) and the energy of α -particles (4.8 MeV), $G[\text{Np(V)}]$ was found to be $6.4 \text{ ion (100 eV)}^{-1}$.

The processes occurring during α -radiolysis are the same as those occurring during γ -radiolysis. The theoretical reduction yield [achieved when the reducing radicals, precursors of H_2 , are completely trapped from spurs by Np(VI)] is 5.8 or $6.5 \text{ ion (100 eV)}^{-1}$, depending on which $G_{\text{H}_2\text{O}_2}$ value (from Table 2 or from Ref. 108) has been used for calculations.

Reduction of Np(VI) (present in a concentration of 1.5×10^{-3} to $1 \times 10^{-2} \text{ mol litre}^{-1}$) in solutions of perchloric acid induced by the α -radiation from ^{244}Cm has been studied.¹⁰⁸ It was shown that owing to the low content of Np(VI) and to the high acidity, the reaction of Np(VI) with H_2O_2 occurs slowly; therefore, it does not come to an end at the instant when the concentrations of Np(VI) and Np(V) are measured. For example, for a solution containing $1.5 \times 10^{-3} \text{ mol litre}^{-1}$ of Np(VI) and $1.0 \text{ mol litre}^{-1}$ of HClO_4 (and for a dose rate of 2.25 Gy s^{-1}), the reduction yields found at the moment of measurement and after the completion of the reaction are 1.6 and $3.5 \text{ ion (100 eV)}^{-1}$, respectively.

Under the action of α -particles, Np(IV) in aerated solutions of perchloric acid is oxidised to Np(V) {at $[\text{HClO}_4] < 1 \text{ M}$] or to Np(VI) {at $[\text{HClO}_4] > 1 \text{ M}$ }.¹⁰⁷ The oxidation yields are 0.8 to $1.8 \text{ ion (100 eV)}^{-1}$ depending on the concentrations of the acid and Np(IV) .

During α -radiolysis of aerated solutions of Np(IV) in which $[\text{HClO}_4] < 1 \text{ M}$, H reacts with O_2 , Np(IV) reacts with OH , HO_2 , H_2O_2 and e_{aq}^- and Np(III) reacts with Np(V) . The partial trapping of reducing radicals in the spurs by Np(IV) ions (their concentration is fairly high) should also be taken into account. Therefore, the yield of Np(IV) can be found from the equation:

$G[-\text{Np(IV)}] = 3(G_{\text{H}} + G_{\text{HO}_2}) + G_{\text{OH}} + 2G_{\text{H}_2\text{O}_2} - G_{e_{\text{aq}}^-} - 2QG_{\text{H}_2}$, (5) where Q is a coefficient characterising the proportion of reducing radicals trapped by Np(IV) ions in the spurs.

The minimum oxidation yield should be obtained when the reducing radicals in the spurs are completely trapped by Np(IV) ions. This is equal to ~ 0.9 – $1.2 \text{ ion (100 eV)}^{-1}$.

When solutions of Np(V) in 4 – 6 M HClO_4 are exposed to α -radiation, an 'induction period' is observed;¹⁰⁷ during this period, Np(VI) ions do not appear but small amounts of Np(IV) are formed.

The transformations of Np(IV) and Np(VI) ions induced by α -radiation in solutions of nitric acid have been studied repeatedly.^{1,4} Both Np(IV) and Np(VI) are converted into Np(V) under the action of α -particles. The yields attained in these processes are listed in Table 17.

The reduction yield of Np(VI) during α -radiolysis of its solutions containing nitric acid is basically determined by the same reactions as in the case of γ -radiolysis. The calculated yield

Table 17. The reduction yields of Np(VI) and oxidation of Np(IV) in α -radiolysis of aerated nitric-acid solutions of neptunium (concentration of neptunium $\sim 10^{-3} \text{ mol litre}^{-1}$).^{1,4}

$[\text{HNO}_3]$ /M	G /ion (100 eV) ⁻¹	$[\text{HNO}_3]$ /M	G /ion (100 eV) ⁻¹
Reduction, dose rate 2.7×10^{-3}		Oxidation, dose rate 2.7×10^{-2}	
1.0×10^{-3}	3.0–3.2	5.0×10^{-3}	2.3
1.0×10^{-2}	5.0	1.0×10^{-2}	2.6
0.1	6.0	5.0×10^{-2}	3.0
0.5	6.6 ^a	0.1	3.4
1.0	5.7 ^a	0.3	3.8
2.0–2.1	4.2	0.5	4.2
		1.0	4.0

^a For these data no dose rate is given in Ref. 4.

for a $1 \times 10^{-3} \text{ M}$ solution of HNO_3 amounts to $3.4 \text{ ion (100 eV)}^{-1}$, which is close to the experimental value.¹ When the concentration of HNO_3 is increased to $\sim 0.5 \text{ M}$, the $G[-\text{Np(VI)}]$ value increases to $6.6 \text{ ion (100 eV)}^{-1}$. This is due to the fact that the nitrate ions suppress the formation of H_2 in the spurs. When this process is suppressed completely, $G[-\text{Np(VI)}]$ should be equal to $6.2 \text{ ion (100 eV)}^{-1}$. The reasons for the decrease in the yield at $[\text{HNO}_3] \geq 1 \text{ M}$ are the same as in the case of γ -radiolysis.

Oxidation of Np(IV) in a $1 \times 10^{-3} \text{ M}$ solution of HNO_3 should proceed *via* its reactions with OH , HO_2 and H_2O_2 . Besides, Np(IV) ions can be reduced by the radicals (precursors of H_2) that they trap in the spurs. As the concentration of HNO_3 increases, nitrate ions trap more and more reducing radicals in the spurs; therefore, the yield should decrease. However, owing to the low dose rate, the reaction between HNO_2 and hydrogen peroxide occurs slowly; H_2O_2 is mostly consumed for oxidation of Np(IV) , and thus the yield of the process increases.

Study of the behaviour of neptunium ions in solutions of nitric acid exposed to larger dose rates of α -radiation created by ^{244}Cm has shown^{109,110} that in 0.11 M HNO_3 , Np(VI) is totally reduced to Np(V) ; however at higher concentrations of the acid (0.33 and 0.62 M), steady states are established, both Np(VI) and Np(V) being present in the solution. In a 1.1 M solution of HNO_3 and at a radiation dose of 30 – 40 kGy , Np(IV) appears. When the dose rate or the concentration of the acid increases, the content of Np(IV) also increases. An increase in the dose rate results in a decrease in the reduction yield. For example, in a solution containing $0.62 \text{ mol litre}^{-1}$ of HNO_3 and $2.3 \times 10^{-3} \text{ mol litre}^{-1}$ of Np(VI) , $G[-\text{Np(VI)}]$ diminishes from 3.5 to $2.2 \text{ ion (100 eV)}^{-1}$ as the dose rate increases from 1.65 to 4.56 Gy s^{-1} ; evidently, this is due to the reaction between HNO_2 and H_2O_2 .¹⁰⁹

On exposure to the same type of radiation, Np(IV) is oxidised to give Np(V) and Np(VI) . When the radiation dose is sufficiently large, Np(IV) in solutions with $[\text{HNO}_3] < 1 \text{ M}$ is totally oxidised

yielding Np(V) (80%–95%) and Np(VI).¹⁰⁹ The oxidation yield diminishes following an increase in the dose rate. Thus in a solution containing $0.75 \text{ mol litre}^{-1}$ of HNO_3 and $\sim 2 \times 10^{-3} \text{ mol litre}^{-1}$ of Np(IV), the $G[-\text{Np(IV)}]$ value diminishes from 1.4 to 0.4 ion $(100 \text{ eV})^{-1}$ as the dose rate increases from 0.65 to 4.9 Gy s^{-1} . This is caused by acceleration of the reaction between HNO_2 and H_2O_2 . In solutions with $[\text{HNO}_3] > 1 \text{ M}$, steady states for Np(IV), Np(V) and Np(VI) are established. As the concentration of the acid increases, the proportions of Np(IV) and Np(VI) increase, while that of Np(V) decreases.¹¹²

The possibility of computer modelling of the changes in the oxidation states of neptunium ions during α - and γ -radiolysis in solutions in nitric acid has been shown.^{111–116} A scheme consisting of 26 reactions was composed; with the use of experimental radiation-chemical yields and the known rate constants for some reactions, this scheme made it possible to describe adequately the radiolytic oxidation of Np(IV) and Np(V) and also the reduction of Np(VI) and Np(V) in 1–6 M solutions of HNO_3 .

Measurement of the solubility of Np(IV) and Np(V) hydroxides in a 5.3 M solution of NaCl has shown that upon prolonged storage of this system, the solubility of Np(IV) hydroxide increases with time, owing to α -radiolysis.¹¹⁷ The solubility of the samples of Np(IV) and Np(V) hydroxides was found to be 10^{-5} – 10^{-6} M at pH 8–13.

3. γ -Radiolysis of alkaline aqueous solutions of neptunium ions

The development of a radiolytic method for the preparation of heptavalent neptunium, plutonium and americium is an important achievement in the radiation chemistry of aqueous solutions. Heptavalent actinides are formed upon irradiation of alkaline solutions of hexavalent actinide ions in the presence of acceptors of hydrated electrons.

The radiolytic method for the preparation of Np(VII) was developed by Pikaev *et al.*^{118,119} It consists in the γ -irradiation of an alkaline (in 1 M NaOH) solution of Np(VI) ($2 \times 10^{-4} \text{ mol litre}^{-1}$) saturated with N_2O . Dinitrogen oxide reacts with e_{aq}^- to give O^- radical ions. In the absence of N_2O , the hydrated electron reduces the Np(VII) formed and reacts with Np(VI). Apart from N_2O , $\text{S}_2\text{O}_8^{2-}$, $\text{H}_3\text{IO}_6^{2-}$, BrO^- and BrO_4^- ions have also been used as scavengers for hydrated electrons. The characteristic features of the method, the yields of Np(VII) under various experimental conditions and the mechanism of oxidation have been considered in detail previously.¹

The rate constant for the reaction of Np(VII) with Np(V) has been estimated by pulse radiolysis.⁵⁴ It is equal to $\sim 2 \times 10^7 \text{ litre mol}^{-1} \text{ s}^{-1}$ in 0.033–2.0 M solutions of LiOH. In solutions of NaOH, this reaction occurs more slowly.

When hydrogencarbonate or carbonate solutions of Np(VI) ($2 \times 10^{-4} \text{ mol litre}^{-1}$) saturated with N_2O or solutions containing $0.1 \text{ mol litre}^{-1}$ of $\text{K}_2\text{S}_2\text{O}_8$ are subjected to γ -radiolysis, no Np(VII) is formed.⁵³ A slight quantity of Np(VII) arises in a 0.5 M solution of Na_2CO_3 containing $0.01 \text{ mol litre}^{-1}$ of NaOH. An increase in the concentration of NaOH to $0.02 \text{ mol litre}^{-1}$ results in the accumulation of $3 \times 10^{-5} \text{ mol litre}^{-1}$ of Np(VII); in a 0.03 M solution of NaOH, almost all the Np(VI) is converted into Np(VII). In this case, the formation of Np(VII) in the presence of N_2O occurs without any 'induction period', Np(VI) being completely converted into Np(VII) at a radiation dose of $\sim 600 \text{ Gy}$. The yield of Np(VII) increases from 0.7 to 4.8 ion $(100 \text{ eV})^{-1}$ following an increase in the concentration of NaOH from 0.02 to 0.1 M, and then somewhat decreases {to 4.1 ion $(100 \text{ eV})^{-1}$ at $[\text{NaOH}] = 1 \text{ M}$ }. Obviously, the reaction of Np(VI) with CO_3^- plays an important role in these systems.

Neptunium(VI) is not oxidised in carbonate-containing solutions. This can be explained by the high redox potential of the Np(VII)/Np(VI) pair and also by the fact that Np(VI) exists as $\text{NpO}_2(\text{CO}_3)_3^{4-}$ under these conditions.⁵³ When the solution is alkalinised, $(\text{NpO}_4 \cdot n\text{H}_2\text{O})^{2-}$ ions appear in it, and they react with

CO_3^- radical ions. Apparently, the oxidation process consists in the transfer of an electron from Np(VI) to CO_3^- .

Irradiation of aerated alkaline solutions of Np(VII) gives rise to Np(VI) ions.¹ If the radiation rate is larger than 300 Gy and $[\text{NaOH}] = 0.5$ – 1 M , the reduction yield is 2.2 to 2.4 ion $(100 \text{ eV})^{-1}$. This is in agreement with the calculated value, which is equal to 2.2 ion $(100 \text{ eV})^{-1}$.

Reduction of Np(VI) and Np(V) in aerated alkaline solutions under the action of γ -radiation of ^{60}Co has been studied.^{120,121} It was found that Np(VI) is reduced to Np(V) and then to Np(IV). The reduction yield hardly depends on the concentration of alkali over the range of concentrations studied (0.9 to $8.5 \text{ mol litre}^{-1}$) and amounts to 1.4–1.6 ion $(100 \text{ eV})^{-1}$ (for radiation doses smaller than 650 Gy). However, the yield diminishes upon an increase in the dose.

The yield markedly increases in the presence of organic substances acting as acceptors of O^- radical ions. In a 2 M solution of NaOH containing $0.013 \text{ mol litre}^{-1}$ of ethylenediaminetetraacetate ions, the yield is 8.5 ion $(100 \text{ eV})^{-1}$ (for a dose of 109 Gy). If the solution contains $1.5 \text{ mol litre}^{-1}$ of NaOH and $0.26 \text{ mol litre}^{-1}$ of formate ions, $G[-\text{Np(VI)}] = 5.8 \text{ ion (100 eV)}^{-1}$ (for doses of $\leq 250 \text{ Gy}$). When carbonate ions are introduced in the solution, the yield barely changes. No reduction of Np(VI) is observed in the presence of nitrite or nitrate ions under low radiation doses (up to 2–3 kGy). However, when the doses are relatively high (more than 10 kGy), a peroxo-complex of Np(V) is formed in solutions containing NO_3^- .^{63,120,121}

Irradiation of aerated alkaline solutions of Np(V) results in the formation of Np(IV) as the corresponding hydroxide, which precipitates from the solution.

It should be noted that γ -radiolysis of alkaline aqueous solutions of Np(V), Np(VI) or their mixtures is accompanied by specific oscillations.^{120–122} They are manifested as a periodical variation of the optical density of the solution. Initially (at low doses), the optical density decreases owing to radiolytic reduction, and then increases due to the light scattering caused by the formation of a finely dispersed suspension. When the irradiated solution is allowed to stand for several hours, the suspension coagulates to give a precipitate, and the optical density decreases. Repeated irradiation results again in the formation of a finely dispersed suspension, and the optical density thus increases. These oscillations of the optical density can be observed until neptunium is entirely reduced to Np(IV).

The mechanism of reduction includes reactions of neptunium ions with e_{aq}^- , O_2^- , and HO_2^- and partial reverse oxidation of the reduced ions with O^- and O_3^- radicals. Based on this mechanism, the following equations were obtained:^{120,121}

$$G[-\text{Np(VI)}] = G[\text{Np(V)}] = G_{e_{\text{aq}}} + G_{\text{H}} + 2G_{\text{H}_2\text{O}_2} - G_{\text{OH}}, \quad (6)$$

$$G[-\text{Np(VI)}] = G[\text{Np(IV)}] = \frac{1}{2}(G_{e_{\text{aq}}} + G_{\text{H}} + 2G_{\text{H}_2\text{O}_2} - G_{\text{OH}}). \quad (7)$$

In all probability, Eqn. (6) is valid for the reduction of Np(VI) to Np(V), while Eqn. (7) holds for the reduction of Np(VI) to Np(IV).

For solutions containing 1 mol litre^{-1} of an alkali, the yields of the products of water radiolysis at pH 12–13 (see Table 1) can be used to calculate the reduction yields from Eqns (6) and (7). In this case, these yields amount to 2.2 ion $(100 \text{ eV})^{-1}$ [for the reduction to Np(V)] and 1.1 ion $(100 \text{ eV})^{-1}$ [for the reduction to Np(IV)]. The value of 1.4–1.6 ion $(100 \text{ eV})^{-1}$ given above for doses below 650 Gy indicates that at these doses, both Np(V) and Np(IV) are produced.

The increase in the reduction yields for solutions containing ethylenediaminetetraacetate or formate ions is due to the interaction of these substances with the O^- radical ions to give organic radicals that act as reducing agents and reduce an additional amount of Np(VI). For these systems, Eqns. (6) and (7) are transformed into the following expressions:

$$G[-\text{Np(VI)}] = G[\text{Np(V)}] = G_{e_{\text{aq}}} + G_{\text{H}} + G_{\text{OH}} + 2G_{\text{H}_2\text{O}_2}, \quad (8)$$

$$G[-\text{Np(VI)}] = G[\text{Np(IV)}] = \frac{1}{2}(G_{e_{\text{aq}}} + G_{\text{H}} + G_{\text{OH}} + 2G_{\text{H}_2\text{O}_2}). \quad (9)$$

The substitution of the numerical values should give the yields equal to 8.0 [for the reduction to Np(V)] and 4.0 ion (100 eV)⁻¹ [for the reduction to Np(IV)]. The value found experimentally for a solution containing ethylenediaminetetraacetate is close to that calculated from Eqn. (8); thus, at low radiation doses, Np(VI) in this system is reduced only to Np(V). The yield found for a solution containing formate ions [5.8 ion (100 eV)⁻¹ for doses below 250 Gy] implies that in this case, Np(VI) is reduced to give both Np(V) and Np(IV).^{120, 121}

The formation of a peroxo-complex of Np(V) in solutions containing nitrate ions is due to the fact that the products of radiolytic transformations of NO₃⁻ protect the arising Np(V) from reverse oxidation (with O⁻ and O₃⁻ radical ions) to Np(VI) and from its subsequent reduction to Np(IV) [apparently, the product of reaction between NO₃⁻ and e_{aq}⁻ is not able to reduce Np(VI)].⁶³ Thus, after a sufficient quantity of Np(V) has been accumulated and the greater part of Np(VI) has been consumed, the possibility for the interaction of Np(V) with H₂O₂ appears.

The reduction of Np(V) in aerated alkaline solutions occurs *via* its reaction with hydrated electrons. Since Np(IV) is poorly soluble in alkali and precipitates from alkaline solutions, its reverse oxidation with O⁻ and O₃⁻ radical ions proceeds at a slow rate, if at all. Hydrated electrons also react with oxygen in this system; however, O₂⁻ (and obviously HO₂⁻) are unable to reduce Np(V). The O⁻ and O₃⁻ radical ions partially oxidise Np(V) to Np(VI) and also react with hydrogen peroxide and with O₂⁻.

VI. Plutonium

Transformations of plutonium ions in solutions of mineral acids induced by X-ray-, γ - and α -radiations have been studied by many researchers. The interest in these processes is caused by the fact that, after dissolution, plutonium reacts with the products of radiolysis of the solvent (water and acids) resulting from the action of the radiation of fission-product elements and actinides. The fact that the redox potentials for pairs of plutonium ions in various oxidation states are close to one another accounts for their simultaneous existence in solutions. This fact should be taken into account during isolation, purification and preparation of plutonium compounds.

1. γ -Radiolysis of acidic aqueous solutions of plutonium ions
Radiolytic transformations of plutonium ions induced by X-ray or γ -radiation and high-energy electrons have been studied in solutions of various acids. Radiolysis has been investigated for solutions of Pu(VI), Pu(IV) and Pu(III), solutions containing plutonium in several oxidation states and solutions containing plutonium together with uranium.

In a study¹²³ (see also Ref. 1) of the behaviour of Pu(VI) ions in 0.2–0.5 M solutions of HClO₄ under the action of γ -radiation from ⁶⁰Co, it has been found that for solutions containing 4.3 × 10⁻³ mol litre⁻¹ of Pu(IV) and 0.2 mol litre⁻¹ of HClO₄, the reduction yield immediately after irradiation (with a dose of ~7.5 kGy) amounted to 0.8 ion (100 eV)⁻¹; this corresponds to the following equation:

$$G[-\text{Pu(VI)}] = G_{e_{aq}^-} + G_H - G_{OH}.$$

Twenty four hours later the reduction yield in the same solutions was 2.3 ion (100 eV)⁻¹. The theoretical yield is equal to:

$$G[-\text{Pu(VI)}] = G_{e_{aq}^-} + G_H + 2G_{H_2O_2} - G_{OH}.$$

Ten days after irradiation the yield was 1.2 ion (100 eV)⁻¹. The equation for the theoretical yield is the following:

$$G[-\text{Pu(VI)}] = \frac{1}{2}(G_{e_{aq}^-} + G_H + 2G_{H_2O_2} - G_{OH}).$$

The dissimilar reduction yields measured within various periods after irradiation are due to the occurrence or absence of the reaction of Pu(VI) with H₂O₂ and to disproportionation of the Pu(V) formed. It should be noted that when the radiation dose is high and the solution is kept after irradiation for a long period,

Pu(III) appears. This is due to the reaction between Pu(IV) and Pu(V) and also, possibly, to the reduction of Pu(IV) with hydrogen peroxide (*via* the formation of a peroxide complex). The results of the γ -radiolysis of deaerated solutions of Pu(VI) are similar to those obtained for aerated solutions.

During the γ -radiolysis of solutions of Pu(III) in 0.2 and 0.5 M HClO₄, no plutonium ions in other oxidation states are accumulated.^{1, 123} In these solutions, oxidation of Pu(III) and reduction of Pu(IV) completely counterbalance each other.

When aerated solutions of 4 × 10⁻³ mol litre⁻¹ of Pu(IV) and 1 × 10⁻³ mol litre⁻¹ of Pu(III) in 0.2 and 0.5 M HClO₄ are exposed to γ -radiation, Pu(III) is accumulated.^{1, 123} The Pu(IV) ions are reduced by H atoms, e_{aq}⁻, HO₂ and H₂O₂ (*via* the intermediate formation of a peroxide complex). The OH radicals participate in the oxidation of Pu(IV).

When a solution containing 3.6 × 10⁻⁴ mol litre⁻¹ of plutonium in 0.3 M HClO₄ (and apparently saturated with nitrogen) has been exposed to X-ray radiation, only oxidised [Pu(V) and Pu(VI)] and reduced [Pu(III) and Pu(IV)] forms of plutonium ions have been distinguished.¹ Under the action of this kind of radiation, plutonium can be reduced or oxidised depending on the ratio of the oxidised and reduced forms in the initial solution. In solutions containing plutonium and uranium, both reduction and oxidation of plutonium ions occur. The yield and the degree of reduction increase with an increase in the concentration of U(VI), the process occurring at the expense of U(V).

The behaviour of plutonium ions in solutions containing sulfuric acid is markedly influenced by the formation of complexes with sulfate ions. This process results in a decrease of the formal redox potentials of the Pu(VI)/Pu(V) and Pu(IV)/Pu(III) pairs; therefore, hydrogen peroxide no longer reduces Pu(IV) but, instead, it mostly oxidises Pu(III). In this case, disproportionation of Pu(V) occurs more rapidly.

The results concerning the radiolytic reduction of Pu(VI) in solutions of sulfuric acid and obtained in a number of studies have been discussed in the previous monograph.¹ The reduction yields vary from 1.2 to 2.5 ion (100 eV)⁻¹ depending on the concentrations of Pu(VI) and sulfuric acid and also on the dose rate. The yields decrease with an increase in the concentration of sulfuric acid or sulfate ions and with a decrease in the concentration of Pu(VI). The mechanism of radiolytic transformations is identical to that for solutions in perchloric acid.

During γ -radiolysis of both aerated and deaerated 1 × 10⁻³ mol litre⁻¹ solutions of Pu(III) in 0.4 M H₂SO₄, Pu(III) is oxidised to Pu(IV).¹ In the case of aerated solutions, post-radiation slow oxidation of Pu(III) with the hydrogen peroxide resulting from radiolysis is observed. The initial yields of Pu(IV) and H₂O₂ are 6.6 ion (100 eV)⁻¹ and 4.0 molecule (100 eV)⁻¹, respectively; this is in agreement with the calculated values. In deaerated solutions containing 10⁻⁴–10⁻³ mol litre⁻¹ of Pu(III), the yields of Pu(IV) and H₂ are 5.5 and 3.6 molecule (100 eV)⁻¹.

In 0.2 M HCl, hexavalent plutonium is reduced to pentavalent plutonium.¹²³ When the radiation dose is ~29 kGy, the reduction yield amounts to 0.56 equivalents (100 eV)⁻¹. The resulting Pu(V) disproportionates to give Pu(IV) and Pu(VI). The yield attained in a 0.5 M solution of HCl is somewhat lower. In hydrochloric acid, OH radicals are consumed, and Cl₂⁻ radical ions arise instead. The latter participate in the oxidation of Pu(V). Trapping of OH radicals or their precursors from the spurs by chloride ions decreases G_{H₂O₂}, increases G_{OH} and decreases G[-Pu(VI)]. Irradiation of a 4 × 10⁻³ mol litre⁻¹ solution of Pu(III) in 0.5 M HCl gives rise to Pu(IV), which is formed as a peroxide complex or as a polymer. Radiolytic oxidation of Pu(III) to Pu(IV) in a deaerated 0.8 M solution of HCl during γ -radiolysis occurs with a yield of 4–5 ion (100 eV)⁻¹ at a radiation dose of ~1 kGy or 0.7 ion (100 eV)⁻¹ when the radiation dose is above 3.8 kGy.¹ The oxidation yield of Pu(III) in aerated solutions of hydrochloric acid also decreases following an increase in the dose, which is due to consumption of oxygen and also to reverse reduction of Pu(IV).

Radiolysis of solutions of Pu(III) in hydrochloric acid has been studied under various conditions.¹²⁴ It was found that in a deaerated solution containing $0.8 \text{ mol litre}^{-1}$ of HCl and $1 \times 10^{-3} \text{ mol litre}^{-1}$ of Pu(III), the initial values of $G[\text{Pu(IV)}]$ and $G(\text{H}_2\text{O}_2)$ are $5.0 \text{ ion (100 eV)}^{-1}$ and $0.6 \text{ molecule (100 eV)}^{-1}$, respectively. The yield increases somewhat when $[\text{Pu(III)}] = 10^{-2} \text{ mol litre}^{-1}$. When the radiation doses are 3–5 kGy, a steady state is established, *i.e.* the ratio of the concentrations of Pu(III) and Pu(IV) remains constant. Irradiation of a $1 \times 10^{-3} \text{ mol litre}^{-1}$ solution of Pu(IV) results in the appearance of Pu(III), the initial yields of Pu(III) and H_2O_2 being equal to $0.36 \text{ ion (100 eV)}^{-1}$ and $0.18 \text{ molecules (100 eV)}^{-1}$, respectively. When a solution containing $4.9 \times 10^{-4} \text{ mol litre}^{-1}$ of Pu(III) and $5.2 \times 10^{-4} \text{ mol litre}^{-1}$ of Pu(IV) is exposed to γ -radiation, Pu(III) is oxidised to only a small extent, whereas $G(\text{H}_2\text{O}_2)$ is equal to 0.46 to $0.83 \text{ molecule (100 eV)}^{-1}$.

In a solution of Pu(III) in 0.8 M HCl saturated with oxygen, the yields of Pu(IV) and H_2O_2 are $6.5 \text{ ion (100 eV)}^{-1}$ and $4.0 \text{ molecule (100 eV)}^{-1}$, respectively (they do not depend on the radiation dose up to $\sim 1 \text{ kGy}$).¹²⁴ When the dose is $\sim 2 \text{ kGy}$, the system remains unchanged, while at 4.5 kGy, a peroxide complex of Pu(IV) is formed.¹²⁴ In 9 M HCl saturated with oxygen, Pu(III) is oxidised with an initial yield of $8.2 \text{ ion (100 eV)}^{-1}$.

The majority of studies dealing with the radiation chemistry of aqueous solutions of plutonium are devoted to the radiolysis of its solutions in nitric acid. This is due to the fact that systems containing nitric acid are often used in the processing of irradiated nuclear fuel.

Study of the γ -radiolysis of solutions of Pu(VI) and mixtures of Pu(IV) and Pu(VI) in 0.5 and 1.5 M solutions of HNO_3 has shown that in solutions containing 3×10^{-3} , 5×10^{-3} and $1 \times 10^{-2} \text{ mol litre}^{-1}$ of plutonium, Pu(VI) is not reduced (for radiation doses of up to $\sim 29 \text{ kGy}$). The results obtained by other researchers are somewhat different (see Ref. 1). It was found that when 2×10^{-4} – $2 \times 10^{-3} \text{ mol litre}^{-1}$ solutions of Pu(VI) in 0.001–0.5 M HNO_3 are exposed to γ -radiation, Pu(VI) is consumed. The reduction yields were found to decrease with an increase in the dose rate and in the concentration of HNO_3 . An important role in the systems under consideration belongs to the formation of nitrous acid (upon the reduction of HNO_3 and NO_3^- with H atoms and e_{aq}^-) and its subsequent reactions with Pu(VI) and H_2O_2 as well as to the reverse oxidation of the resulting Pu(V) with NO_3 radicals. The mechanism of radiolysis of nitric acid solutions of Pu(VI) under these conditions has been discussed in detail previously.¹ The influence of the reaction conditions on the reduction yield of Pu(VI) was also considered in the monograph cited. The authors obtained equations describing the dependence of $G[\text{Pu(VI)}]$ on the dose rate and on the concentration of Pu(VI).

The character of the reduction of Pu(VI) in 0.3–8 M (at a dose rate of 2.67 Gy s^{-1}) depends on its concentration.^{125, 126} When $[\text{Pu(VI)}]_0 = 5 \times 10^{-3} \text{ mol litre}^{-1}$, no reduction occurs in the above range of concentrations of HNO_3 up to a dose of 2.4 MGy. When $[\text{Pu(VI)}]_0 = 0.1 \text{ mol litre}^{-1}$, Pu(VI) is reduced to Pu(IV) in 0.3–4 M HNO_3 and is not reduced in 8 M HNO_3 (at a dose of 2.4 MGy). In 0.3–1.0 M solutions of HNO_3 , reduction starts immediately after the beginning of irradiation, whereas in the case of 3–4 M solutions, the process starts after an induction period. The presence of an induction period is also observed in the reduction of a $\sim 5 \times 10^{-2} \text{ mol litre}^{-1}$ solution of Pu(VI) in 1 M HNO_3 and of a $1 \times 10^{-2} \text{ mol litre}^{-1}$ solution of Pu(VI) in 0.3 M HNO_3 .

An induction period is a typical feature of autocatalytic processes. Autocatalytic reduction of Pu(VI) was observed for the first time about 40 years ago during α -radiolysis of nitric acid solutions of Pu(VI). It was suggested that slow accumulation of Pu(V) and its disproportionation give rise to Pu(IV). The latter reacts with HNO_2 and H_2O_2 thus yielding Pu(III), which reduces Pu(VI) and Pu(V).

It has been shown¹²⁵ that when Pu(IV) is added to the starting solution of Pu(VI), the initial rate of reduction of the latter increases and the induction period is shortened. This is true for solutions in which $[\text{Pu(VI)}] > 5 \times 10^{-3} \text{ mol litre}^{-1}$. The addition

of Pu(IV) to a solution in which $[\text{Pu(VI)}] \leq 5 \times 10^{-3} \text{ mol litre}^{-1}$ does not result in acceleration of the reduction; on the contrary, Pu(IV) is oxidised. During γ -radiolysis in HNO_3 solutions, HNO_2 is accumulated.¹²⁵

When Pu(VI) is reduced by nitrous acid, an equilibrium is established. Pu(VI) is consumed in three processes. Firstly, the Pu(V) formed disproportionates. Secondly, Pu(IV) reacts with Pu(V), and the resulting Pu(III), in its turn, reacts with Pu(VI), *i.e.* the corresponding equilibrium is established. Thirdly, Pu(IV) is reduced with nitrous acid, and Pu(III) reacts with Pu(VI) and Pu(V).

The overall rate of reduction of Pu(VI) and the rate of its reduction by nitrous acid were calculated.¹²⁵ The latter was found to be 2–3 times lower than the observed rate. Therefore, it was suggested that Pu(VI) and Pu(IV) are reduced by the precursors of nitrous acid, namely, e_{aq}^- and H. It was also found that the degree of reduction of Pu(VI) depends on its concentration and on the concentration of HNO_3 .

The kinetics of reduction of Pu(VI) for various conditions of γ -irradiation have been calculated.¹²⁷ The results of calculations were in satisfactory agreement with experimental data. However, it has been noted¹²⁸ that for 1 M HNO_3 with $[\text{Pu(VI)}] = 1 \times 10^{-2} \text{ mol litre}^{-1}$ and for 3 M HNO_3 with $[\text{Pu(VI)}] = 0.1 \text{ mol litre}^{-1}$, the reaction of Pu(VI) with hydrogen peroxide should also be taken into account. When deaerated nitric acid solutions of mixtures of Pu(III) and Pu(IV) are exposed to X-rays, Pu(V) and, possibly, Pu(VI) are accumulated. The initial oxidation yield decreases from 0.052 to $\sim 0.004 \text{ ion (100 eV)}^{-1}$ as the concentration of HNO_3 increases from 0.3 to 2 M. The introduction of nitrate ions leads to a decrease in the yield of oxidation.

The behaviour of Pu(IV) ions during γ -radiolysis in nitric acid has been studied in detail.¹²⁹ In a 0.3 M solution of HNO_3 at $[\text{Pu(IV)}]_0 = 1 \times 10^{-3} \text{ mol litre}^{-1}$ [owing to disproportionation of Pu(IV), the solution contained some quantities of Pu(III) and Pu(VI)] and at a dose rate of 2.17 Gy s^{-1} , oxidation of Pu(IV) is observed. When the $[\text{Pu(IV)}]_0$ value is increased to $8 \times 10^{-3} \text{ mol litre}^{-1}$, the oxidation occurs only at the beginning of irradiation, and then reduction of Pu(VI) occurs instead. When the dose rate (I) is equal to 1.33 Gy s^{-1} , reduction of Pu(VI) is also observed. In a 1 M solution of HNO_3 containing $1 \times 10^{-2} \text{ mol litre}^{-1}$ of Pu(IV) at $I = 1.33 \text{ Gy s}^{-1}$, a steady state is established after accumulation of $\sim 1 \times 10^{-3} \text{ mol litre}^{-1}$ of Pu(VI). The process of oxidation in 6 M HNO_3 at $[\text{Pu(IV)}]_0 = 1 \times 10^{-2} \text{ mol litre}^{-1}$ and $I = 2.17 \text{ Gy s}^{-1}$ occurs at a constant rate up to a dose of $\sim 1 \text{ MGy}$. The initial oxidation yields depend on the concentrations of Pu(IV) and HNO_3 and on the dose rate. The concentration of the nitrous acid formed was also measured in the study cited. To estimate the yields of oxidation of Pu(IV), equations were proposed that permit prediction of its behaviour under various conditions.

In a study of γ -radiolysis of solutions of Pu(III) in nitric acid, it has been found that in the case of deaerated solutions, the initial yields of Pu(IV) and HNO_2 are identical and amount to $7.8 \text{ ion (100 eV)}^{-1}$.¹²⁸ In solutions saturated with oxygen, $G[\text{Pu(IV)}] = 8.4 \text{ ion (100 eV)}^{-1}$, whereas $G[\text{HNO}_2]$ is close to zero.

The initial yields of Pu(IV) both in deaerated solutions and in solutions saturated with oxygen are close to the following value:

$$G_{e_{\text{aq}}} + G_{\text{H}} + G_{\text{OH}} + 2G_{\text{H}_2\text{O}_2} = 8.2 \text{ molecule (100 eV)}^{-1}.$$

Evidently, hydrated electrons and H atoms react in this system with nitrate ions and with non-dissociated nitric acid to give NO_3^{2-} and HNO_3^- , respectively; these species are finally converted into NO_2 and N_2O_4 . Nitrogen dioxide and its dimer are able to oxidise Pu(III).¹²⁸ The OH radicals participate in the oxidation of Pu(III) and in the reactions with NO_3^- and HNO_3 to give NO_3 radicals. The latter oxidises Pu(III). Hydrogen peroxide, apparently, reacts slowly with Pu(III), each molecule of the peroxide oxidising two Pu(III) ions (*via* the intermediate formation of OH radicals). In solutions saturated with oxygen, H atoms partly react with oxygen thus yielding HO_2 radicals; each of these radicals is able to oxidise

three Pu(III) ions. Therefore, the initial yield of Pu(IV) in these solutions is somewhat higher than that in deaerated solutions.

In conformity with the proposed mechanism, the initial yield of HNO₂ should be equal to $G_{\text{eq}} + G_{\text{H}} = 3.65$ ion (100 eV)⁻¹. The value found experimentally¹²⁸ for deaerated solutions is markedly higher. However, in solutions saturated with oxygen, the yield of HNO₂ is close to zero.¹²⁸ This casts doubt on its high yield in deaerated solutions.

When the radiation doses are high, the quantity of Pu(IV) formed is sufficient for its reaction with nitrous acid. This should result in a decrease in the yield of Pu(IV), and this is actually observed in the experiment.¹²⁸

The influence of U(VI) ions on the radiolytic transformations induced by X-rays of plutonium ions in deaerated 0.3 M solutions of HNO₃ has been studied.¹ The initial oxidation yield of plutonium was found to decrease from 0.05 ion (100 eV)⁻¹ observed in the absence of U(VI) to zero for solutions containing 0.3 mol litre⁻¹ of U(VI). At higher concentrations of U(VI), plutonium is reduced. The introduction of dichromate ions in U(VI)-containing solutions of plutonium in nitric acid results in oxidation of plutonium accompanied by reduction of Cr₂O₇²⁻. The dependences of the behaviour of plutonium on the ratio of concentrations of hexavalent chromium and uranium, on the concentration of HNO₃ and on the radiation dose were investigated.

Study of radiolytic transformations of Pu(VI) in 3 M HNO₃ in the presence of U(VI) has demonstrated that the introduction of U(VI) shortens the induction period observed for the reduction of plutonium in the absence of uranium ions.¹²⁶ A similar phenomenon was observed in solutions containing Pu(IV) and Pu(VI). It was shown that U(V) resulting from radiolysis reduces Pu(VI) and Pu(IV).

The behaviour of Pu(IV) and Pu(VI) ions in 4 M solutions of HNO₃ exposed to high-energy electron pulses generated by a U-12 linear electron accelerator has been studied.¹³⁰ It was found that, irrespective of the ratio of the concentrations of Pu(IV) and Pu(VI), the dose rate (for medium dose rates of 35–200 Gy s⁻¹) and the temperature (in the range 10–90 °C), the irradiation results in the reduction of Pu(VI) to Pu(IV). In some cases, $G[-\text{Pu(VI)}]$ is proportional to $I^{-1/2}$; the rate of reduction was found to depend on the temperature. The mechanism of radiolysis of this system has been discussed comprehensively by Tkhorzhnitskii and Egorov,¹³¹ who proposed an equation for the reduction yield of Pu(VI) [or the yield of formation of Pu(IV)]. This equation relates $G[\text{Pu(IV)}]$ to I , $[\text{Pu(V)}]$ and $[\text{Pu(III)}]$. However, the dependence of the yield of Pu(IV) on I found by these researchers differs from that described in a previous study.¹³⁰

To elucidate the role of polyvalent ions in the reduction of plutonium induced by pulse electron radiation, 4 M solutions of HNO₃ containing Pu(VI), Pu(IV), U(VI), Ru, Rh, Pd, Mo, Ce and other elements have been studied.¹³⁰ It was found that Pu(VI) is reduced only when uranium and palladium are present simultaneously. Uranium(VI) increases the 'reducing capacity' over the whole process, whereas Pd(II) is active only at the beginning of the process.¹³¹ On exposure to radiation, U(VI) is converted into U(V), while Pd(II) transforms into Pd(I), Pd(III) and Pd(IV); the latter results from disproportionation of Pd(III). Palladium(IV) is reduced by nitrous acid, U(V), Pd(I), Pu(III), Pu(IV) and Pu(V) to give Pd(II). This accounts for the fact that Pu(IV) is partly oxidised during the radiolysis of its solutions in the presence of Pd(II) but in the absence of U(VI). Note that the reduction yield of Pu(VI) in the presence of U(VI) and Pd(II) decreases with an increase in the radiation dose.

Radiolytic transformations of Pu(VI) in 0.01–0.1 M solution of HNO₃ containing Np(VI) have been studied.¹³² It was found that at a $[\text{Pu(VI)}]/[\text{Np(VI)}]$ ratio of 12.5, both Pu(VI) and Np(VI) are reduced. Plutonium remains in the solution in the hexavalent state at radiation doses below 320 Gy.

The same researchers¹³² studied the reduction of Pu(VI) and oxidation of Pu(IV) in 0.5–4 M solutions of HNO₃ at $[\text{Pu}]/[\text{Np}]$ ratios of 0.005–0.125. When $[\text{HNO}_3] = 0.5$ M, neptunium exists as Np(V), whereas in 2–4 M solutions of HNO₃, some Np(VI) can

also be found in the system. It was found that in 0.5 M HNO₃, the reduction of Pu(VI) in the presence of neptunium occurs when $[\text{Pu}] \geq 5 \times 10^{-4}$ mol litre⁻¹, the rate of the reduction being higher than that in the absence of neptunium. At the same time, in 2–4 M solutions of HNO₃, reduction of Pu(VI) mixed with neptunium is observed at $[\text{Pu}] \geq 10^{-2}$ mol litre⁻¹. The reduction of Pu(VI) starts after an induction period corresponding to a 75%–80% reduction of Np(VI). The reduction yield depends on the concentration of plutonium and does not depend on the concentration of HNO₃. In the absence of neptunium, the rate of reduction decreases with an increase in the concentration of the acid.

Radiolytic oxidation of Pu(IV) in the presence of neptunium in 0.5 M HNO₃ has been studied.¹³³ It was found that the smaller the concentration of plutonium, the larger its proportion being oxidised. In the presence of Pu(VI), the rate of oxidation decreases. After prolonged irradiation, steady-state concentrations of Pu(VI) and Pu(IV) are established. The mechanism for the γ -radiolysis of this system was proposed, equations were derived and the concentrations of Pu(VI) at various doses were calculated.¹³³

2. α -Radiolysis of acidic aqueous solutions of plutonium ions

In the majority of cases, α -radiolysis of plutonium induced by its own radiation has been studied. Sometimes α -radiolysis results in the oxidation of plutonium; however, most often it leads to a decrease in its average oxidation number.

As early as the 1940–1950s it was found¹ that the rate of reduction of Pu(VI) induced by α -radiation in 0.48–1.9 M solutions of HClO₄ containing either only Pu(VI), or Pu(VI) + Pu(IV), or Pu(VI) + Pu(IV) + Pu(V) obeys zero-order kinetics, the rate constant k being equal to 1.18×10^{-2} days⁻¹. The reduction yield is expressed by the following equation

$$G[-\text{Pu(VI)}] = k(100T_{1/2}/0.693E), \quad (10)$$

where $T_{1/2}$ is the half-life of the corresponding plutonium isotope (days) and E is the average energy of α -particles (eV).

The half-life of ²³⁹Pu is 2.411×10^4 years, $E = 5.106$ MeV (11.8%), 5.144 MeV (15%) and 5.157 MeV (73%).¹³⁴ It follows from Eqn. (10) that $G[-\text{Pu(VI)}] = 2.92$ ion (100 eV)⁻¹.

Under the action of its own α -radiation, Pu(VI) is reduced to Pu(V); the latter disproportionates. The Pu(IV) thus formed reacts with Pu(V) to give Pu(III) and Pu(VI).¹ Reduction of Pu(VI) in 0.2 M HClO₄ under the action of α -particles emitted by ²¹⁰Po has been studied.¹²³ When the radiation dose is lower than 3 kGy, Pu(V) forms in the solution, and $G[-\text{Pu(VI)}] = 3.2$ ion (100 eV)⁻¹. When the dose is higher than 3 kGy, Pu(IV) is formed, and $G[-\text{Pu(VI)}] = 1.6$ ion (100 eV)⁻¹. Finally, when the dose exceeds 11 kGy, Pu(III) is accumulated, and $G[-\text{Pu(VI)}] = 1.1$ ion (100 eV)⁻¹. These results do not depend on whether or not air is present in the solution. The theoretical yield for the reduction of Pu(VI) to Pu(V) is 3.0 ion (100 eV)⁻¹, which is in agreement with the experimental result.

In a 1 M solution of HClO₄ containing ~ 0.01 mol litre⁻¹ of ²³⁹Pu(IV) (at 25 °C), the average oxidation number of plutonium changes by 0.014 every day until it becomes 3.02–3.05.¹ The gas evolved from the solution consists of oxygen (60%) and hydrogen (40%). The solution was found to contain a substantial amount of chloride ions, which obviously had been formed by the action of ionising radiation on the perchlorate ions. The theoretical reduction yield of Pu(IV), like that for the reduction of Pu(VI), is 3.0 ion (100 eV)⁻¹. The $G[-\text{Pu(IV)}]$ value calculated from an equation similar to Eqn. (10) is 3.5 equivalent (100 eV)⁻¹. The slight difference between these values can be due to the fact that Pu(IV) accepts some of the reducing radicals from the spurs.

The radiolytic transformations of ²³⁸Pu(IV) and ²³⁸Pu(VI) in 1 M HClO₄ have been described.¹³⁵ The radiation dose rate was ~ 0.15 Gy s⁻¹. The concentration of Pu(IV) remained constant, whereas Pu(VI) was reduced to give Pu(IV) and Pu(III). Using the data presented in this study, we calculated that $G[-\text{Pu(VI)}] = \sim 0.16$ ion (100 eV)⁻¹. The reduction yield is so low, because in the 1 M solution of HClO₄, the reaction between Pu(VI) and H₂O₂

occurs slowly; therefore, hydrogen peroxide is accumulated and can react with OH, H and e_{aq}^- in the bulk of the solution and in the spurs.

An increase in the dose rate of α -radiation by 3–4 orders of magnitude somewhat changes the course of radiolysis. Study of the reduction of Pu(VI) in 2 M HClO₄ under the action of the α -particles emitted by ²⁴⁴Cm (at a dose rate of 3.95 Gy s⁻¹) has led to the following results.¹⁰⁸ Initially, the concentration of reduction slowly decreases [we calculated the reduction yield to be 0.01 ion (100 eV)⁻¹], and then, after ~82%–83% of Pu(VI) has been consumed (this takes ~100 h), its concentration starts to increase { $G[\text{Pu(VI)}] = 0.003$ ion (100 eV)⁻¹}.

When a solution of Pu(VI) in a 0.11 M solution of H₂SO₄ is exposed to α -particles, Pu(IV) is formed;¹²³ $G[-\text{Pu(VI)}] = G[\text{Pu(IV)}] = 3$ equivalent (100 eV)⁻¹. The mechanism of reduction is identical to that observed in the case of solutions in perchloric acid. The reduction yield of Pu(VI) barely depends on the concentration of H₂SO₄ as it varies from 0.001 M to 0.3 M and is close to 3 equivalent (100 eV)⁻¹ (see Ref. 1).

It was found¹ that on exposure to α -radiation, Pu(VI) and Pu(IV) ions in 0.06–1.5 M solutions of HCl are reduced at a rate of 1%–0.3% of the average oxidation number per 24 h. Study of the radiolytic reduction of Pu(IV) in a solution of a mixture of HClO₄ and HCl has demonstrated that $G[-\text{Pu(IV)}]$ diminishes as [HClO₄] decreases and as [HCl] increases. For example, in 1 M HClO₄, the yield is 3.5 equivalent (100 eV)⁻¹ whereas in 1 M HCl, it is equal to zero. Plutonium ions in low oxidation states are oxidised in HClO₄ solutions containing 0.1 mol litre⁻¹ of Br⁻. Evidently, this is accomplished *via* the same reactions as the oxidation during α -radiolysis in hydrochloric acid.

Study of the behaviour of ²³⁸Pu(OH)₄ in solutions of NaCl has shown^{135–137} that when [NaCl] is less than 3 M, Pu(IV) is oxidised to Pu(V), while at [NaCl] > 3 M, Pu(IV) is converted into Pu(VI). The mechanism of radiolysis includes trapping of OH radicals from the spurs and the formation of oxidising agents (Cl, Cl₂⁻, HClO, ClO⁻). The yield of H₂O₂ should diminish with an increase in the concentration of NaCl. In solutions containing less than 3 mol litre⁻¹ of NaCl, the yield of H₂O₂ [expressed in equivalent (100 eV)⁻¹] is apparently half that of the oxidising agents. The latter convert Pu(IV) into Pu(V) and Pu(VI); the hexavalent plutonium is reduced by hydrogen peroxide to Pu(V), which is stable in the presence of H₂O₂. In solutions containing more than 3 mol litre⁻¹ of NaCl, the yield of H₂O₂ is low, and thus Pu(VI) is not reduced and is accumulated or is reduced to a small extent.

Radiolytic transformations of plutonium ions in concentrated solutions of NaCl have been studied.¹³⁸ This study was undertaken in view of the intended burial of solid radioactive wastes in depleted salt pits. It was noted that the reaction of PuO₂²⁺ with hypochlorite ions resulting from α -radiolysis of these solutions plays an important role in the process.

In a study of the reduction of Pu(VI) (~7 × 10⁻³ mol litre⁻¹) in solutions of NaNO₃ (the initial pH value was 3), it has been shown that Pu(V) is accumulated initially, and then the process gradually decelerates. At this time, formation of Pu(IV) as a colloid begins. It was found¹ that the $G[-\text{Pu(VI)}]$ value changes from 4.4 to 7.2 ion (100 eV)⁻¹ as the concentration of NO₃⁻ ions increases from 0.1 to 5 mol litre⁻¹. An equation for calculating the theoretical $G[-\text{Pu(VI)}]$ values in these systems was derived, and the calculated values were compared with experimental results.¹

The data on the α -radiolysis of solutions of HNO₃ with concentrations of less than 0.5 mol litre⁻¹ have been discussed in the monograph cited.¹ It was noted that under these conditions, only H₂O₂ is accumulated. It has been calculated¹³⁹ that in a 0.4 mol litre⁻¹ solution of ²³⁹Pu (at a dose rate of 2.7 × 10⁻³ Gy s⁻¹), the rate of formation of H₂O₂ is equal to 2 × 10⁻⁶ mol (litre h)⁻¹, and over a period of 30 days the concentration of Pu(VI) should decrease by ~25%. However, this does not occur in reality, because after 30 days, the induction period is completed. The low initial rate of reduction of Pu(VI), present in a concentration of less than 0.01 mol litre⁻¹ in HNO₃ solutions, is presumably due to its reverse oxidation by nitrous acid.¹³⁹

The reduction of Pu(VI) in solutions of nitric acid induced by its own α -radiation has been studied by many investigators.^{1, 139–143} The following characteristic features of this process are noteworthy.

Reduction in solutions with pH 3.8 at [Pu(VI)] = 8 × 10⁻³ mol litre⁻¹ is characterised by an induction period. In more dilute solutions, Pu(VI) is reduced without an induction period. The initial reduction yields vary from 4 to 6 equivalent-s (100 eV)⁻¹.¹ In 1–4 M solutions of HNO₃, Pu(VI) is reduced to Pu(IV);¹⁴¹ in more dilute solutions of nitric acid, Pu(III) is also formed.^{1, 139} When [HNO₃] is more than 0.5 M, α -radiolysis of solutions of Pu(VI) is accompanied by accumulation of HNO₂. The introduction of Pu(IV) shortens the induction period but has only a slight influence on the maximum rate of reduction of Pu(VI).^{1, 139}

It has been found¹⁴¹ that in 4–6 M solutions of HNO₃, plutonium remains in the tetravalent state for several years if the dose rate of α -radiation does not exceed 0.3 Gy s⁻¹. At higher dose rates, Pu(VI) is accumulated. The yield of Pu(VI) depends on the concentration of HNO₃; as it increases from 0.9 to 9 M, the yield decreases from 0.0013 to 0.0008 ion (100 eV)⁻¹. An increase in the dose rate also decreases the yield of Pu(VI). In the opinion of the researchers cited,¹⁴¹ Pu(IV) is oxidised *via* the reactions with OH radicals and nitrogen oxides; hydrogen peroxide acts as a reducing agent. The decrease in the rate of reduction upon an increase in the concentration of HNO₃ was explained by the formation of a complex of Pu⁴⁺ with nitrate ions.

The behaviour of Pu(VI) and Pu(IV) in nitric acid solutions exposed to intense α -radiation has been investigated in greater detail in other studies.^{1, 142, 143} In 6 M solutions of HNO₃ containing up to 0.1 mol litre⁻¹ of Pu(IV) under a dose rate of 4.6 Gy s⁻¹, Pu(VI) is accumulated; the rate of its formation gradually decreases, and finally a steady state is established. The initial rate of oxidation depends linearly on the concentration of Pu(IV). In solutions containing less than 1.8 × 10⁻² mol litre⁻¹ of Pu(VI), no reduction occurs over a period of 40 days; at [Pu(VI)] = 1.8 × 10⁻² mol litre⁻¹, reduction occurs to only a slight extent.¹⁴² When some Pu(IV) is introduced into solutions of Pu(VI), Pu(VI) is reduced to a noticeable extent but not entirely: steady-state concentrations of Pu(IV) and Pu(VI) are established.¹⁴⁰ According to our estimate, the yields of oxidation of Pu(IV) at [Pu(IV)]₀ ≈ 2 × 10⁻³ mol litre⁻¹ are 0.019 and 0.022 equivalent (100 eV)⁻¹ for 1 and 6 M HNO₃, respectively.

In a study of the reduction of Pu(VI) in 0.3–6 M HNO₃ exposed to the α -radiation from ²⁴⁴Cm, it has been found that at [HNO₃] > 1 M, Pu(VI) is reduced to Pu(IV); this process starts after an induction period.¹⁴⁰ This period becomes shorter following an increase in the dose rate and in the concentration of Pu(VI) and becomes longer upon an increase in the concentration of HNO₃. According to our estimate, the reduction yield of Pu(VI) is 0.08 equivalent (100 eV)⁻¹ and it does not depend on the dose rate in the range of 0.95–9.2 Gy s⁻¹. In a 0.3 M solution of HNO₃, hexavalent plutonium is reduced to Pu(V), steady-state concentrations of Pu(V) and Pu(VI) being established.

It was found^{142, 143} that, Pu(III) in solutions of nitric acid is oxidised on exposure to α -radiation. Under the action of α -particles emitted by curium ($I = 4.2$ Gy s⁻¹), Pu(III) in 0.12 M HNO₃ is partly oxidised to Pu(IV), which forms a peroxide complex. In addition, small amounts of Pu(VI) are accumulated. The degree of conversion of Pu(III) is 20%, and the initial oxidation yield is 3.8 ion (100 eV)⁻¹. When the concentration of HNO₃ increases, the rate and the degree of conversion of Pu(III) increases, and at [HNO₃] > 1 M, trivalent plutonium is completely transformed into the tetravalent state. No peroxide complex is formed in solutions containing more than 0.5 mol litre⁻¹ of HNO₃. When [HNO₃] = 2.9 M, the oxidation yield reaches 74 ion (100 eV)⁻¹, which indicates that a chain process occurs. The introduction of nitrite ions causes a slight increase in the rate of oxidation. The addition of sulfamic acid, which binds HNO₂, decelerates the oxidation or even completely terminates it.

In our opinion, in a 0.12 M solution of HNO_3 , nitrate ions trap almost all the reducing radicals from the spurs. Therefore, OH and HO_2 radicals and nitrous acid act as the main oxidants for plutonium(III), *i.e.*:



If we substitute the yields of the products of water radiolysis (see Table 2) in Eqn. (11), we obtain an oxidation yield equal to 3.9 ion $(100 \text{ eV})^{-1}$, which coincides with the experimental result.^{142, 143}

When the concentration of HNO_3 increases, the yield of oxidants decreases owing to the reaction between HNO_2 and H_2O_2 ; however, HNO_2 (or NO, according to another reaction scheme) reduces nitric acid and thus a chain process develops leading to high oxidation yields. Sulfamic acid binds not only HNO_2 but, apparently, also the oxidising radicals, namely, OH and NO_3 . Therefore, oxidation slows down or even stops.

A series of studies^{144–151} have been devoted to the mathematical modelling of processes that occur in solutions of nitric acid containing plutonium ions and exposed to γ - or α -radiation. The influence of various factors on these processes, for example, the concentration of HNO_3 , oxidation states of plutonium and radiation dose rate, was considered. The calculations were based on experimental results obtained for about 30 reactions. The modelling made it possible to interpret the course of the process and the contributions of individual stages. In some cases, the rate constants for the reactions were estimated; however, they did not always coincide with the values measured experimentally.

Study of the α -radiolysis of solutions of Pu(VI) and Np(VI) in nitric acid has shown that Pu(VI) is not reduced until all the Np(VI) present has been reduced.¹³¹ To elucidate the mechanism of the process, a set of differential equations based on kinetic regularities were composed and numerical integration with known initial conditions was carried out. Comparison of experimental results demonstrated that the period of 'retention' of Pu(VI) depends on the $[\text{Pu(VI)}]_0/[\text{Np(VI)}]_0$ ratio. The main feature characterising the radiolysis in the system under consideration is that Np(VI) is reduced more rapidly. The decrease in the rate of reduction of Pu(VI) in the presence of Np(VI) was explained not only by the fact that the latter reacts faster with hydrogen peroxide and with nitrous acid but also by the fact that Np(VI) reacts with Pu(V).

Study of the radiolysis of solutions of nitric acid containing Np(IV) and Pu(IV) induced by the α -radiation of ^{244}Cm has shown that the initial rates of accumulation of Np(V) and consumption of Pu(IV) differ from those for systems containing only Np(IV) or Pu(IV).¹⁵² In particular, it was noted that the rate of oxidation of Np(IV) increases, (among other reasons) due to oxidation of Np(IV) by Pu(IV) ions. A model for the radiolysis in this system was proposed and the redox processes occurring in the system were described using 42 reactions.

3. Gas evolution in the radiolysis of acidic solutions of plutonium ions

During some technological operations involving aqueous solutions of plutonium in nitric acid, the formation of explosive gas mixtures is possible. Primary attention in the study of gas evolution during radiolysis is paid to prevention of the formation of these mixtures. Before 1980, gas evolution during radiolysis had been measured many times. In the case of α -radiolysis, gases are formed in markedly higher yields than upon γ -radiolysis.¹

α -Radiolysis of solutions of plutonium ($0.188–0.42 \text{ mol litre}^{-1}$) in 1–9.9 M HNO_3 has been found to be accompanied by the formation of hydrogen, oxygen, nitrogen, dinitrogen oxide and nitrogen monoxide (hydrogen is the component formed in the highest yield). The yields decrease from 0.2 to 0.018 molecule $(100 \text{ eV})^{-1}$ as the concentration of HNO_3 increases from 1 to 9.9 M. The yields of oxygen for these concentrations are 0.082 and ~ 0 molecule $(100 \text{ eV})^{-1}$. The yields of nitrogen, dinitrogen oxide and nitrogen monoxide in a 9.7 M solution of HNO_3 are equal to 0.043, 0.0031 and 6×10^{-4} molecule $(100 \text{ eV})^{-1}$, respectively.

Several samples of a 8.5 M solution of HNO_3 containing $\sim 1 \text{ mol litre}^{-1}$ of Pu(IV) have been stored for 52 months. Gases were formed in the following average yields, molecule $(100 \text{ eV})^{-1}$: $G(\text{the sum of gases}) = 0.060$, $G(\text{H}_2) = 0.033$, $G(\text{O}_2) = 0.021$, $G(\text{N}_2) = 0.005$; traces of nitrogen oxides were also detected.

The decrease in the concentration of hydrogen upon an increase in the concentration of HNO_3 (and, obviously, plutonium ions) is due to trapping of reducing radicals from the spurs, which suppresses the formation of hydrogen. Molecular oxygen arises upon the direct action of the radiation on NO_3^- and HNO_3 and also upon the reactions of H_2O_2 and HO_2 with plutonium ions [mostly with Pu(IV)]. In 1 M HNO_3 , the yield of O_2 resulting from the direct action can be neglected. The $G(\text{O}_2)$ value is much smaller than $G_{\text{H}_2\text{O}_2}$; this is due to the reaction between HNO_2 and H_2O_2 . As the concentration of HNO_3 increases, the rate of this reaction increases; therefore, $G(\text{O}_2)$ decreases. Nitrogen and its oxides appear upon direct action of the radiation on NO_3^- and HNO_3 .

We calculated $G(\text{H}_2)$ values for the α -radiolysis of solutions of Pu(IV) (50 g litre^{-1}). For solutions in 1 M HNO_3 , 1 M HClO_4 and 0.1 M H_2SO_4 , the following values were found, molecule $(100 \text{ eV})^{-1}$: 0.21, 0.38 and 1.6, respectively. In our opinion, the fact that the yields attained in HNO_3 and HClO_4 are smaller than that in H_2SO_4 can be explained in the following way. In a dilute solution of H_2SO_4 , Pu(IV) ions form sulfato-complexes, which react with e_{aq}^- and H more slowly than the aqua-complex. In addition, in solutions of sulfuric acid, Pu(III) is oxidised by the H atoms, and this process affords H_2 . In HNO_3 and HClO_4 solutions, plutonium ions accept more precursors of H_2 from the spurs than in H_2SO_4 .

An equation has been reported,¹⁵³ which permits the calculation of the amount of hydrogen evolved from highly radioactive wastes containing, among other components, nitrates and plutonium. The yields of hydrogen evolved by plutonium-containing brines under the action of α -particles emitted by ^{239}Pu vary from 0.6 to 1.5 molecule $(100 \text{ eV})^{-1}$ depending on the composition of the brine.¹⁵⁴ It has been noted¹⁵⁵ that the yield of hydrogen in the α -radiolysis of nitrate-containing solutions of plutonium almost does not depend on the form [Pu(IV) or Pu(VI)] in which plutonium occurs in the system.

4. Radiolysis of alkaline aqueous solutions of plutonium

During γ -radiolysis of aerated alkaline solutions of Pu(VI), plutonium is first reduced to Pu(V) and then to Pu(IV).^{63, 156} The reduction yield is 1.5–1.6 ion $(100 \text{ eV})^{-1}$, irrespective of the concentration of alkali, over the concentration range studied (1 to 6 M). As in the case of γ -radiolysis of alkaline aqueous solutions of Np(VI), specific 'oscillations' in the variation of the optical density of the solution exposed to radiation are observed. The oscillations include an initial decrease in the intensity of absorption of Pu(VI) caused by its reduction to Pu(V), its subsequent increase caused by the formation of a fine suspension and light scattering from its particles, a further decrease in the absorption intensity caused by precipitation, *etc.* However, as distinguished from γ -radiolysis of alkaline solutions of Np(VI), in this case, no peroxide complex of Pu(V) was detected in nitrate-containing solutions; this is due to the low stability of this complex.

The mechanism of radiolytic transformations of Pu(VI) in aerated alkaline solutions is similar to that for Np(VI). The main distinction is that the Pu(V) resulting from reduction disproportionates to give Pu(IV) and Pu(VI).^{63, 156}

Radiolysis of alkaline aqueous solutions of Pu(VI) in the presence of acceptors of radical reducing agents transforming them into radicals acting as oxidants affords Pu(VII) ions. This was observed for the first time by Pikaev *et al.*¹¹⁸ In this study, alkaline solutions of Pu(VI) saturated with dinitrogen oxide were exposed to radiation. As noted above, dinitrogen oxide reacts with e_{aq}^- yielding the O^- radical anion. More recently, oxidation of Pu(VI) has been studied more comprehensively.¹⁵⁷ With allowance for the induction effect, the initial yield of Pu(VII) in a 1 M solution of NaOH was equal to 5.4 ion $(100 \text{ eV})^{-1}$. The mechanism of radio-

lytic oxidation of Pu(VI) in alkaline solutions is similar to that for Np(VI).

The formation of Pu(VII) has also been observed^{158, 159} in the γ -radiolysis of aerated solutions of Pu(VI) in 1 M NaOH in the presence of $\text{S}_2\text{O}_8^{2-}$. It was found that $G[\text{Pu(VII)}] = 4.0 \text{ ion (100 eV)}^{-1}$ at $[\text{Pu(VI)}] = 5.1 \times 10^{-4}$ and $[\text{S}_2\text{O}_8^{2-}] = 0.07 \text{ mol litre}^{-1}$. This value is close to the yield of Np(VII) obtained in a 1 M solution of NaOH containing $\text{S}_2\text{O}_8^{2-}$ ions. These ions react with e_{aq}^- , and the $\text{S}_2\text{O}_8^{3-}$ ion radicals thus formed react with OH^- and are finally converted into O^- . The experimental $G[\text{Pu(VII)}]$ value is lower than the calculated value [$\sim 4.7 \text{ ion (100 eV)}^{-1}$]; this is apparently due to the occurrence of side reactions of O_3^- ion radicals (resulting from the reaction of O^- with O_2) and/or $\text{S}_2\text{O}_8^{3-}$ ion radicals. When $[\text{Pu(VI)}] = 5 \times 10^{-3} \text{ mol litre}^{-1}$, the yield of Pu(VII) amounts to $\sim 2 \text{ ion (100 eV)}^{-1}$. The decrease in the yield compared to that attained in more dilute solutions of Pu(VI) is due to the fact that in an alkaline medium the stability of the $\text{S}_2\text{O}_8^{3-}$ ion radicals can be relatively high and sufficient for them to react partly with Pu(VI).

The irradiation of aerated alkaline solutions of Pu(VII) results in its reduction.¹⁵⁷ The reduction yield does not depend on the concentrations of Pu(VII) (the concentration range used was $2.4 \times 10^{-4} - 1 \times 10^{-3} \text{ mol litre}^{-1}$) or the alkali (in the range 0.87–3.5 M); it is $2.35 \text{ ion (100 eV)}^{-1}$. The mechanism of the process has been discussed previously.¹

The behaviour of Pu(IV) and Pu(VI) in 1–15 M solutions of NaOH containing nitrate ions has been studied.¹⁶⁰ The solutions were irradiated for 2 years by α -particles emitted by plutonium. Initially, Pu(V) was accumulated in the solution over the precipitate of Pu(IV) hydroxide and then its amount decreased. The decrease in the concentration of Pu(V) began after 1–2, 7, 20 and 56 days in 1, 2–9, 10 and 15 M solutions of NaOH, respectively.

The researcher cited¹⁶⁰ did not discuss what oxidising and reducing agents could have been involved in the reactions in this system. He attributed the decrease in the concentration of Pu(V) to a change in the degree of crystallinity of Pu(IV) hydroxide. In our opinion, two processes occur in this system, namely, oxidation of Pu(IV) in the precipitate and reduction of Pu(V) in the bulk of the solution. The oxidation is accomplished by O^- radical ions and hydroperoxide HO_2^- . Note that HO_2^- is able to oxidise freshly precipitated Pu(IV) hydroxide.¹⁶¹ The reduction of Pu(V) might be accomplished by e_{aq}^- , H and NO_3^{2-} ion radicals (resulting from reactions of e_{aq}^- and H with nitrate ions). According to our estimates, $G[-\text{Pu(V)}]$ decreases from 15.5 to $2.6 \text{ ion (100 eV)}^{-1}$ as the concentration of NaOH increases from 1 to 15 M. These high yields may be associated not only with Pu(V) ions but also with plutonium in a colloidal form.

Hexavalent plutonium introduced in alkaline solutions is gradually reduced.¹⁶¹ The initial reduction yields, which we have determined using the data about the variation of the concentration of Pu(VI) reported by Delegard,¹⁶⁰ decrease from 25.2 to $2.6 \text{ ion (100 eV)}^{-1}$ as the activity of NaOH increased from 0.6 to 3.4 M. If we assume that the yields of the products of the α -radiolysis of water in alkaline solutions are equal to those in sulfuric or perchloric acid, the theoretical reduction yield of Pu(VI) to Pu(V) should be $\sim 3 \text{ ion (100 eV)}^{-1}$. The higher values could be due to the presence of organic impurities and/or co-precipitation of Pu(VI) with Pu(V). As time goes on, some Pu(V) in the precipitate is converted into Pu(IV); therefore, the colour of the precipitate changes.¹⁶⁰

VII. Americium

1. γ -Radiolysis of aqueous solutions of americium ions

The studies performed before 1980 dealt with γ -radiolysis of weakly acidic solutions of Am(III) saturated with dinitrogen oxide and solutions of Am(VI) in nitric or in phosphoric acid and alkaline solutions of Am(VI). The most significant results are presented in Table 18.

The method of pulse radiolysis with fast recording of short-lived species has been used to elucidate the mechanism of radiolytic oxidation of Am(III).^{52, 165} It was found that short-lived Am(IV) ions are formed intermediately in this process; these ions were identified based on the broad optical absorption band with a maximum at 340 nm, which appears under the action of an electron pulse. Based on the accumulation of Am(IV), the rate constants for the reaction of Am(III) with OH under various conditions were measured (see Table 6). This reaction has also been studied by pulse radiolysis (see, for example, Refs 30 and 166).

In solutions of Am(III) saturated with N_2O , Am(IV) ions are consumed in a second-order reaction. For $[\text{Am(III)}]_0 > 2 \times 10^{-3} \text{ mol litre}^{-1}$, this reaction was found to be disproportionation of Am(IV). The rate constants for this process ($2k$ values) at pH 2.0 and pH 2.6–3.2 are 4.5×10^6 and $6 \times 10^6 \text{ litre mol}^{-1} \text{ s}^{-1}$, respectively.⁵² According to another study,³⁰ at pH 5.2, the $2k$ value is $1.0 \times 10^7 \text{ litre mol}^{-1} \text{ s}^{-1}$. When the concentration of

Table 18. Yields of products in the radiolytic transformations of americium in aqueous solutions.¹

Ameri- cium	Radi- ation	Medium		G /ion(100 eV) ⁻¹
		I	II	
Oxidation to Am(V)				
Am(III)	γ	HClO ₄ , satu- ration with N ₂ O	(~4.0)	0.85
	α	K ₂ CO ₃	3.0–5.5	—
	α	NaCl	5.0 (8.3)	0.6 ^a
Reduction to Am(III)				
Am(IV)	α	H ₃ PO ₄	10	—
Am(IV), ^b	α	HClO ₄	(2.0–4.0)	4.4
	α	HNO ₃	0.4	8.8
Am(IV)	α	NH ₄ F	13.0	~4.0
Am(V)	α	HClO ₄	0.1–2.0	1.2–2.3
	α	H ₂ SO ₄	1.0	1.4
	α	HNO ₃	0.5–9.0	0.019–0.61 ^c
	α	HCl	0.5	1.74
	α	HClO ₄ + H ₃ PO ₄	0.1 + 0.01	1.7
Reduction to Am(V)				
Am(VI)	α	HNO ₃	0.1–4.7	3.0–4.0
	α	HNO ₃	See ^d	3.3–64.0
	α	HClO ₄	0.2–6.0	3.0–4.0
	α	HClO ₄	12.0	0
	α	H ₂ SO ₄	0.1–10.0	1.2–4.0
Reduction to Am(III)				
	γ	H ₃ PO ₄	3.0	2.2
	α	H ₃ PO ₄	3.0 and 10.0–11	1.0–2.3 1.2–4.0
Reduction to Am(V)				
Am(VI)	α	NaHCO ₃ or K ₂ CO ₃	—	4.0
Reduction to Am(IV)				
Am(VI), ^b	α	K ₁₀ P ₂ W ₁₇ O ₆₁	(3.0–8.0) × 10 ⁻³	0.35 ^e
Oxidation to Am(VII)				
Am(VI)	γ	NaOH, in the presence of N ₂ O or S ₂ O ₈ ²⁻	1.0–3.0	—

^a The yield was estimated from the data of Ref. 162. ^b Complex with $\text{P}_2\text{W}_{17}\text{O}_{61}^{10-}$. ^c The yields were estimated from the data of Ref. 163. ^d The medium changed from a solution with pH 3.1 to a 14.3 mol litre⁻¹ solution of HNO_3 . ^e The yields were estimated from the data of Ref. 164.

Am(III) is lower, in addition to the disproportionation of Am(IV), its reactions with HO_2 and H_2O_2 occur in the system.

In aerated solutions, Am(IV) also disappears through a second-order reaction. This is the interaction of Am(III) with HO_2 . The rate constants measured for this process are listed in Table 14. It can be seen that the rate constant depends on the pH of the solution. This was explained by the fact that Am(IV) ions are hydrolysed to different extents at different pH values.

The rate constant for the reaction of Am(IV) with hydrogen peroxide was measured (see Table 9). An attempt has been made⁵² to determine the rate constant for the reaction between Am(IV) and Am(V). According to an approximate estimate, the upper limit for this rate constant is $3 \times 10^4 \text{ litre mol}^{-1} \text{ s}^{-1}$.

Pulse radiolysis experiments^{30, 31, 166} indicate that the reaction of e_{aq}^- with Am(III) affords Am(II). It is responsible for an absorption band with a maximum at 310 nm³¹ or 312 nm.³⁰ The rate constants found for this reaction are listed in Table 3. The intensity of the optical absorption of this ion decreases with a decrease in the pH of the solution. The Am(II) ion is unstable. At pH 4.7, it disappears with a half-life of 70 μs .³¹ When the concentration of Am(III) is large and the dose per pulse is low, Am(II) reacts with water.³⁰ The rate constant for this reaction is $9.7 \times 10^4 \text{ s}^{-1}$.

The results obtained using pulse radiolysis made it possible to propose a mechanism for the oxidation of Am(III) in the γ -radiolysis of its weakly acidic solutions saturated with N_2O . This mechanism has been discussed in detail previously.¹

The transformations of Am(VI) ions during the γ -radiolysis have been studied in aqueous solutions containing nitric or phosphoric acid and also in alkaline solutions. In the latter case, irradiation was used to obtain Am(VII).

Based on the possible mechanism of the radiolytic transformations of Am(VI) in nitric acid solutions exposed to γ -radiation, an equation for $G[-\text{Am(VI)}]$ has been derived.¹ Calculations in terms of this equation led to yields of 5.0 and 5.3 ion (100 eV)⁻¹ for 0.1 and 1 M solutions of HNO_3 , respectively. This is close to experimental results. For a 4.7 M solution of HNO_3 , this equation cannot be used, because in this case, the direct action of the ionising radiation on HNO_3 and NO_3^- should be taken into account.

In the radiolysis of solutions of Am(VI) in phosphoric acid, the H_2PO_4 radical, which is an oxidant, plays an important role.¹⁶⁷ Therefore, it cannot be ruled out that this radical, like OH radical, can oxidise the Am(V), Am(IV) and Am(III) ions formed. However, these oxidation reactions might be slow, and recombination of $\text{H}_2\text{PO}_4^\cdot$ to give $\text{H}_4\text{P}_2\text{O}_8$ can compete with them. This provided grounds for the conclusion that the theoretical yield should lie in the range $0.77 \leq G[-\text{Am(VI)}] \leq 1.4 \text{ ion (100 eV)}^{-1}$. The experimental value is much higher. The possible reasons for this discrepancy have been discussed in the previous monograph.¹

Under certain conditions, γ -radiolysis of alkaline solutions of Am(VI), like that for neptunium and plutonium, yields Am(VII). Dinitrogen oxide and $\text{S}_2\text{O}_8^{2-}$ have been used as scavengers for hydrated electrons (see Table 18).¹⁶⁸ The details of the procedure for preparing Am(VII) as well as the mechanism of the oxidation have been considered in the monograph.¹

2. α -Radiolysis of aqueous solutions of americium ions

Radiolysis of aqueous solutions of americium induced by its own α -radiation has been studied in various media: in nitric, sulfuric, hydrochloric and phosphoric acids, in carbonate-containing solutions, in the presence of sodium bromate, in 'unsaturated' phosphotungstic acids, etc. Radiolytic transformations of Am(VI), Am(V) and Am(III) ions in solutions of perchloric acid have also been studied. With allowance for the possible mechanism of the reduction of Am(VI) in perchloric acid, one can calculate its theoretical yield; it is equal to 3.0 ion (100 eV)⁻¹. This result is in agreement only with some of the values found experimentally (see Table 18). The scatter of experimental values for the yields is caused by the use of solutions of different degrees

of purity. The reduction of Am(VI) with water contributes somewhat to the process.¹⁶⁹ The decrease in $G[-\text{Am(VI)}]$ to 0 in 12 M HClO_4 can be explained by the change in the yields of the products of water radiolysis and by the sharp retardation of the reaction between Am(VI) and H_2O_2 .

As Am(V) accumulates in the solution, its reduction by the HO_2 radical or e_{aq}^- becomes possible. Hydrogen peroxide does not react with Am(V) until Am(VI) is fully consumed.

The data on the radiolytic behaviour of Am(VI) presented in Table 18 have been obtained at a dose rate of α -radiation lower than 0.2 Gy s^{-1} . α -Radiolysis of solutions of Am(VI) in 0.1–11 M HClO_4 at a dose rate of 0.01 – 4.6 Gy s^{-1} has been studied.¹⁷⁰ In this study, ^{244}Cm was used as the source of α -radiation. The initial reduction yield in a 0.13 M solution of HClO_4 ($I = 2.9 \text{ Gy s}^{-1}$) is $3.1 \text{ ion (100 eV)}^{-1}$. When the concentration of the acid is increased to 0.5–1 M, the yield decreases somewhat, but when the concentration becomes larger than 2 M, the yield of reduction increases: in a 7 M solution of HClO_4 , it is $\sim 48 \text{ ion (100 eV)}^{-1}$. Obviously, such a high yield is due to the presence of organic impurities.

In the case of 0.2 M solutions of HClO_4 containing variable amounts of NaClO_4 , the yield increases monotonically with an increase in the concentration of NaClO_4 and reaches $5.5 \text{ ion (100 eV)}^{-1}$ at $[\text{NaClO}_4] = 7 \text{ mol litre}^{-1}$.¹⁷⁰ The reduction yield was found to depend somewhat on the concentration of Am(VI). When the concentration of HClO_4 is 1 M, the yield does not depend on the dose rate; however, in a 5.5 M solution of HClO_4 , it is proportional to I^2 .

It is noteworthy that the increase in the reduction yield at high concentrations of HClO_4 or NaClO_4 , among other reasons, is due to the fact that Am(VI) reacts with the products of radiolytic decomposition of the perchlorate ion. In particular, it has been found¹⁷¹ that Am(VI) ions are reduced at a relatively high rate when ClO_2 is passed through a solution of Am(VI) in perchloric acid.

In a study of Kornilov *et al.*,¹⁷¹ $G[-\text{Am(VI)}]$ was shown to be independent of the concentration of Am(VI), which is at variance with an earlier study.¹⁷⁰ In fact, in 0.5 M HClO_4 , the yield is equal to 2.3 – $2.5 \text{ ion (100 eV)}^{-1}$ in the range of Am(VI) concentrations of $(1.5$ – $6) \times 10^{-3} \text{ mol litre}^{-1}$.

During the α -radiolysis in perchloric acid solutions, Am(V) is reduced to Am(III) (see Table 18). An equation for $G[-\text{Am(V)}]$, which is equal to $G[\text{Am(III)}]$, has been obtained¹ with allowance for the mechanism of radiolysis of Am(V) in perchloric acid. Using this equation, it was found that the theoretical yield amounts to $1.5 \text{ ion (100 eV)}^{-1}$. Experimental values are close to this result. The fact that the yield increases somewhat at high concentrations of Am(V) ions is due to the fact that these ions trap the reducing radicals from the spurs.

It has been found¹⁷² that prolonged storage of weakly acidic saturated solutions of NaClO_4 containing Am(III) and Cm(III) results in the formation of precipitates. The quantity of the precipitate increases with time, and the colour changes from light brown to black. The time required for the formation of the precipitates decreases with an increase in the dose rate. The optical absorption spectrum of the solution above the precipitate exhibits bands typical of Am(V) (4%) and of the products of radiolytic decomposition of ClO_4^- ions. The solution changes from weakly acidic to neutral. X-ray diffraction analysis has shown that the precipitates contain NaCl (80%), NaClO_3 (20%) and americium and curium hydroxides. The precipitates were dissolved, and it was found that $\sim 30\%$ of americium in them occurred in the pentavalent state.

Several researchers have studied α -radiolysis of solutions of Am(VI) in sulfuric acid. The values found for the reduction yields of $^{241}\text{Am(VI)}$ vary from 1.2 to $4.0 \text{ ion (100 eV)}^{-1}$ (see Table 18). Probably, the processes occurring in the α -radiolysis of solutions of Am(VI) in sulfuric acid and in perchloric acid are the same. In this case, the theoretical $G[-\text{Am(VI)}]$ value should be $3.0 \text{ ion (100 eV)}^{-1}$. The differences between the experimental

and calculated values are apparently caused by the same reasons as in the case of solutions in perchloric acid.

It should be noted that the $G[-\text{Am(VI)}]$ values obtained for concentrated solutions of sulfuric acid are smaller than those for dilute solutions. This can be explained by the fact that HSO_4^- ions and sulfuric acid partially trap the OH radicals from the spurs and, hence, the $G_{\text{H}_2\text{O}_2}$ value decreases. The HSO_4^- (or SO_4^-) radicals are oxidants and they, like OH radicals, can oxidise the Am(V) formed.

Pentavalent americium is reduced in solutions of sulfuric acid under the influence of α -radiation (see Table 18). In a solution containing 1 mol litre $^{-1}$ of H_2SO_4 , Am(V) is first consumed at a constant rate, and then the rate decreases.

In the case of solutions in nitric acid, the reduction of Am(VI) and Am(V) as well as the influence of $\text{S}_2\text{O}_8^{2-}$ and BrO_3^- ions on the stability of Am(VI) towards α -radiolysis have been studied. The reduction of Am(VI) during the α -radiolysis in nitric acid includes the same reactions as that during γ -radiolysis. With allowance for this fact, an equation for $G[-\text{Am(VI)}]$ has been derived.¹ Application of this equation to a 0.5 M solution of HNO_3 leads to a theoretical yield of 4.74 ion (100 eV) $^{-1}$. The experimental $G[-\text{Am(VI)}]$ values found by various researchers differ fairly markedly from one another (see Table 18). Apparently, this is due to insufficient purity of the solutions used in some of the studies.

Study of the behaviour of Am(VI) in solutions of HNO_3 and LiNO_3 under the action of the α -radiation of ^{244}Cm has shown¹⁷³ that at $[\text{HNO}_3] \leq 6$ M, Am(VI) is reduced to Am(V) [up to the instant when Am(VI) disappears, not more than 4% of Am(III) is accumulated]. At $[\text{HNO}_3] > 6$ M, the amount of the Am(III) formed increases. This is due to disproportionation of Am(V). The reduction yields of Am(VI) markedly increase in the presence of LiNO_3 . According to our estimates, in a 2.9×10^{-3} M solution of Am(VI) containing 0.01 mol litre $^{-1}$ of HNO_3 and 1 mol litre $^{-1}$ of LiNO_3 , the yield is equal to 48 ion (100 eV) $^{-1}$. If $[\text{LiNO}_3] = 9.1$ M, $G[-\text{Am(VI)}] = 75.5$ ion (100 eV) $^{-1}$. In all probability, the so high yields are due to the presence of nonidentified impurities in the solution.

In solutions containing nitric acid, Am(V) is reduced under the influence of α -particles to Am(III) (see Table 18). The reduction yield of Am in 0.01 M HNO_3 almost does not differ from those obtained in dilute HClO_4 or H_2SO_4 . When $[\text{HNO}_3]$ is increased to 4.5 M or $[\text{LiNO}_3]$ is increased to 1 M, the interaction of nitrate ions with reducing radicals starts to contribute to the process; therefore, the reduction yield of Am(V) decreases. In 6–9 M HNO_3 , disproportionation of Am(V) becomes significant; hence, the observed reduction yield increases.

Study of α -radiolysis of solutions of Am(VI) in nitric acid containing $\text{S}_2\text{O}_8^{2-}$ ions has shown that at a constant concentration of HNO_3 , the reduction yield of Am(VI) decreases upon an increase in the concentration of $\text{S}_2\text{O}_8^{2-}$. Conversely, when the concentration of $\text{S}_2\text{O}_8^{2-}$ is constant, $G[-\text{Am(VI)}]$ increases with an increase in the concentration of HNO_3 . A detailed interpretation of these findings has been reported previously.¹

As in the case of Am(VI), $\text{S}_2\text{O}_8^{2-}$ ions have an influence on the stability of Am(V) ions during the α -radiolysis in solutions of nitric acid. The reduction yields of Am(V) obey complex dependences on the concentrations of Am(V), HNO_3 and $\text{S}_2\text{O}_8^{2-}$ and on the dose rate. The introduction of bromate ions into a nitric acid solution of Am(V) decreases the rate of its reduction during α -radiolysis.

Pentavalent americium is reduced during the α -radiolysis in hydrochloric acid (see Table 18). The reduction occurs *via* reactions with HO_2 , H_2O_2 and with hydrogen atoms resulting from the radiolysis of water and interaction with e_{aq}^- . Chloride ions react with OH radicals in the bulk of the solution and partly in the spurs (in the latter case, this reaction decreases $G_{\text{H}_2\text{O}_2}$). The Cl_2^- radical ions arising from the interaction of OH with Cl^- can both oxidise Am(V) and react with H_2O_2 (in the latter case, OH is formed). The resulting Am(VI) is reduced by hydrogen peroxide and by chloride ions.

The behaviour of Am(III) in concentrated solutions of NaCl under the action of α -radiation has been studied.^{136, 162} Radiolytic

transformations of Am(III) in a 5 M solution of NaCl at pH 8.3 was investigated.¹⁶² Americium(V) is formed as the final product of α -radiolysis. The mechanism of radiolysis includes the interaction of OH with Cl^- (formation of Cl_2^-) and, in the opinion of the researcher,¹⁶² the formation of HClO . The ion ClO^- and, perhaps, Cl_2^- act as oxidising agents. The reactions of Cl_2^- with Am(V) and H_2O_2 as well as reactions of Am(VI) with H_2O_2 and Cl^- can occur in this system.

In phosphoric acid, reduction of Am(VI), Am(V) and Am(IV) has been studied (see Table 18). We shall consider the most significant results of these studies. As in the case of γ -radiolysis, Am(VI) is reduced to Am(III); $G[-\text{Am(VI)}]$ is almost independent of the concentration of H_3PO_4 but decreases following an increase in the dose rate. The mechanism of reduction of Am(VI) during the α -radiolysis includes the same reactions as that during γ -radiolysis. As in the case of γ -radiolysis, the yields found experimentally are markedly higher than the calculated values; the possible reasons for this are also the same.

Some studies have dealt with the stability of the complex of Am(IV) with phosphotungstate (see Table 18). The stability of the complex of Am(IV) with $\text{P}_2\text{W}_{17}\text{O}_{61}^{10-}$ depends on the pH and on the concentration of the phosphotungstate ion. Erin *et al.*¹⁶⁴ believe that Am(IV) is reduced both radiolytically and by water. Study of the stability of Am(VI) in solutions of $\text{P}_2\text{W}_{17}\text{O}_{61}^{10-}$ has shown¹⁷⁴ that Am(VI) is converted into Am(IV). According to our estimates, the $G[-\text{Am(VI)}]$ values vary from 3.3 to 0.35 ion (100 eV) $^{-1}$ as the pH changes from 0 to 6.

VIII. Other actinides

Data on the radiolysis of aqueous solutions of transamericium elements are scarce. This is due to the fact that these elements are relatively unavailable and are characterised by short half-lives. Some information about the radiolysis of solutions containing curium, berkelium and californium ions have been reported.

1. Solutions of curium ions

Several studies have been devoted to α -radiolysis of aqueous solutions of Cm(IV) in the presence of complex-forming agents. It has been found¹ that in a 15 M solution of CsF at 10.5°C, $^{244}\text{Cm(IV)}$ is reduced under the action of its own α -radiation to Cm(III), the rate constant for reduction and the $G[-\text{Cm(IV)}]$ value being equal to 2.17×10^{-4} s $^{-1}$ and 3.08 ion (100 eV) $^{-1}$, respectively. The reduction yield of Cm(IV) should be determined by its reactions with H , e_{aq}^- , HO_2 and H_2O_2 and by the reverse oxidation of the resulting Cm(III) by the OH radical. Unfortunately, since there are no data on the yields of the primary products of α -radiolysis of concentrated aqueous solutions of fluoride ions, it is impossible to calculate the theoretical reduction yield of Cm(IV) and to compare it with the experimental value.

The stability of Cm(IV) prepared by oxidation of Cm(III) on heating with peroxodisulfate in the presence of $\text{K}_{10}\text{P}_2\text{W}_{17}\text{O}_{61}$ has been studied.^{1, 175} At room temperature (without removal of the oxidant), Cm(IV) is reduced to Cm(III); the yield is 2.63 ion (100 eV) $^{-1}$.

In the presence of the oxidant, the rate of the process in the initial period [before the Cm(IV) is reduced by $\sim 50\%$] is constant; then a deviation from the linear dependence is observed. For the initial period, $G[-\text{Cm(IV)}]$ is 4.74 ion (100 eV) $^{-1}$. In another study, a complex of Cm(IV) with phosphotungstate has been used.¹⁷⁵ It was found that the consumption of Cm(IV) as well as that of Am(IV) or Cf(IV) obeys the equation

$$-\frac{d[\text{An(IV)}]}{dt} = k_0 + k_1[\text{An(IV)}], \quad (12)$$

where k_0 is the rate of the radiation-chemical process.

The reduction yield estimated from the k_0 value is more than 20 ion (100 eV) $^{-1}$ (in the pH range of 1.5–6.1 and at a concentration of the heteropolyanion of 0–0.012 mol litre $^{-1}$). In the studies under consideration, the concentration of phosphotung-

state exceeded the concentration of curium; therefore, e_{aq}^- and H should react mostly with the heteropolyanion to give 'heteropoly-blue'. The rate constant for the corresponding reaction of e_{aq}^- is $\sim 1.2 \times 10^{11}$ litre mol $^{-1}$ s $^{-1}$.⁵ Therefore, it cannot be ruled out that heteropolyanions accept the precursors of H₂ from the spurs. Evidently, the heteropoly-blue reacts with Cm(IV). The reduction yield can be found from the equation

$$G[-\text{Cm(IV)}] = G_{e_{aq}^-} + G_H + G_{\text{HO}_2} + 2G_{\text{H}_2\text{O}_2} + 2AG_{\text{H}_2} - G_{\text{OH}}, \quad (13)$$

where A is the factor characterising the decrease in the yield of hydrogen caused by trapping of its precursors by heteropolyanions in the spurs.

In the limiting case, the reduction yield of Cm(IV) in α -radiolysis can reach 5.8 ion (100 eV) $^{-1}$. The high yields reported by Kuno *et al.*¹⁵⁵ are most likely caused by the presence of organic impurities.

Deaerated solutions of Cm(III) containing perchlorate ions and *tert*-butyl alcohol (added as an acceptor of the OH radicals) have been studied by pulse radiolysis.¹⁶⁶ It was found that upon the passage of an electron pulse, an optical absorption with a maximum at 240 nm appears. This absorption was attributed to Cm(III) arising in the reaction with e_{aq}^- . However, the large negative redox potential of the Cm(III)/Cm(II) pair casts doubt upon this interpretation. In a solution saturated with N₂O, the action of an electron pulse gives rise to optical absorption with a maximum at 260 nm. This was assigned to Cm(IV) resulting from the reaction of Cm(III) with OH radicals.

2. Solutions of berkelium ions

Oxidation of Bk(III) induced by γ -radiolysis has been studied in a biphasic system consisting of a 6 M aqueous solution of HNO₃ and a 0.2 mol litre $^{-1}$ solution of di(2-ethylhexyl) phosphate (DEHP) in decane.¹⁷⁶ It was found that upon irradiation, berkelium is converted almost entirely into the tetravalent state and is extracted into the organic phase. In this system, Bk(III) is oxidised by NO₃ radicals. The resulting Bk(IV) is partially reduced by nitrous acid and is partially extracted into the organic phase.

In a solution containing 2 mol litre $^{-1}$ of K₂CO₃, trivalent berkelium is oxidised to Bk(IV) under the influence of its own β -radiation. The half-transformation period is 2.5 h, which corresponds to $G[-\text{Bk(III)}] = 5.45$ ion (100 eV) $^{-1}$. The mechanism of the process has been considered in the monograph.¹ Based on this mechanism, an equation for $G[\text{Bk(IV)}]$ was obtained; the theoretical yield found from this equation is 8.2 ion (100 eV) $^{-1}$. The experimental result is markedly smaller. It is most likely that, owing to the low concentration of Bk(III), the radicals acting as oxidants are not completely consumed in the reactions with Bk(III) and participate in side processes (for example, they react with H₂O₂ and/or O₂ $^-$).

By virtue of pulse radiolysis, the formation of Bk(II) has been observed upon exposure of a deaerated 2.5×10^{-3} mol litre $^{-1}$ solution of Bk(III) containing *tert*-butyl alcohol (pH 5) to an electron pulse.³² The appearance of Bk(II) is due to the reaction of Bk(III) with e_{aq}^- (the rate constant for this reaction is presented in Table 3). The absorption spectrum of Bk(II) has a maximum at 310 nm (the molar extinction coefficient at this wavelength is 230 m² mol $^{-1}$). This ion is short-lived; the rate constant for its disappearance is 1.53×10^5 s $^{-1}$.

The resistance of ²⁴⁹Bk(IV) to its own β -radiation in acidic solutions has been considered in a number of studies (see, for example, Refs 1 and 177–179). In solutions of sulfuric acid, Bk(IV) has been found to be reduced under the influence of its own β -radiation and by water; the $G[-\text{Bk(IV)}]$ values range from 0.83 to 6.5 ion (100 eV) $^{-1}$ and decrease with an increase in the concentration of the acid. In perchloric acid solutions, the reduction yields measured by various researchers vary from 2.4 to 10.2 ion (100 eV) $^{-1}$. The yields of Bk(IV) for several types of solution are listed in Table 19.

The theoretical $G[-\text{Bk(IV)}]$ value can be found based on the mechanism including the reactions of Bk(IV) with H, e_{aq}^- , HO₂ and

Table 19. The yields of reduction of Bk(IV) in β -radiolysis in various media.

10 ³ [Bk(IV)] /mol litre $^{-1}$	Medium		$G[-\text{Bk(IV)}]$ /ion (100 eV) $^{-1}$	Ref.
	I	II		
6.9–12.7	HClO ₄	1.0	2.4	177
4.5	HClO ₄	2.0	2.8	177
3.0	HClO ₄	3.0	2.9	177
2.6	HClO ₄	5.0	3.1	177
4.0	HNO ₃	0.5	4.3	177
2.4	HNO ₃	1.0	4.6	177
3.3	HNO ₃	3.0	5.7	177
2.8	HNO ₃	6.0	5.9	177
6.7×10^{-2}	HNO ₃	9.0	4.7	178
7.0×10^{-2}	HNO ₃	9.0	3.6	178
< 0.1	HNO ₃ + + AgNO ₃ + + (NH ₄) ₂ S ₂ O ₈	4.0 + + 0.01 + + 0.1	0.043	179

H₂O₂ and the reaction of the resulting Bk(III) with OH. The presence of air in the solution exerts no influence on $G[-\text{Bk(IV)}]$, because the HO₂ radical resulting from the reaction of H with O₂, like the H atom itself, reduces one Bk(IV) ion. Taking into account the whole set of reactions, we obtain a $G[-\text{Bk(IV)}]$ value of 2.3 ion (100 eV) $^{-1}$. Experimental values are markedly higher in most cases. Evidently, this is due to the presence of organic impurities in the solutions used. The OH radical reacts with RH₂ present as an impurity. The 'RH' radical thus formed is capable of reducing Bk(IV).

Apparently, the most reliable data have been obtained by Erin *et al.*¹⁷⁷ The authors took into account the experience of the earlier researchers and paid primary attention to the purification of the initial sample of ²⁴⁹Bk. It was shown that consumption of Bk(IV) in solutions containing perchloric or nitric acid obeys zero-order kinetics, *i.e.* Bk(IV) is reduced only *via* reactions with the products of water radiolysis. In 2–5 M HClO₄, reduction is accomplished by e_{aq}^- , H, H₂O₂, HO₂ and by the products of decomposition of ClO₄ $^-$ induced by the direct action of ionising radiation. As a result, the reduction yield is somewhat higher than that in 1 M HClO₄. In nitric acid [as in solutions of Am(VI) with similar compositions], H₂O₂ and HNO₂ act as the reducing agents; some of the Bk(III) thus formed is oxidised again by NO₃ radicals.

The relatively high reduction yields of Bk(IV) in sulfuric acid are obviously caused by the presence of organic impurities. The decrease in $G[-\text{Bk(IV)}]$ following an increase in the concentration can be due to the interaction of HSO₄ $^-$ with OH radicals, which suppresses the reactions of these radicals with RH₂. The HSO₄ (SO₄ $^-$) radicals are able to oxidise Bk(III); however, they react with organic compounds much more slowly than OH radicals. In addition, in concentrated solutions of H₂SO₄, the HSO₄ $^-$ ions partly accept the OH radicals from the spurs, which results in an increase in G_{OH} and a decrease in $G_{\text{H}_2\text{O}_2}$.

β -Radiolysis of solutions of Bk(IV) in mixtures of perchloric and nitric acids and of perchloric acid with lithium nitrate has been studied.¹⁸⁰ As the content of nitrate ions in the solutions increases, $G[-\text{Bk(IV)}]$ increases as has also been observed for solutions in nitric acid containing no HClO₄.

It has been reported¹ that when the biphasic system consisting of a 0.05 mol litre $^{-1}$ solution of DEHP in decane and a 6 M aqueous solution of HNO₃ and containing 1.04×10^{-6} mol litre $^{-1}$ of Bk(IV) and 3.6×10^{-3} mol litre $^{-1}$ of Ce(III) is exposed to α -radiation from ²⁴⁴Cm, Bk(IV) is formed and passes to the organic phase. The maximum degree of oxidation, equal to $\sim 30\%$, is achieved when the radiation dose is ~ 360 kGy (the dose rate is ~ 1.6 Gy s $^{-1}$). The average $G[\text{Bk(IV)}]$ value is ~ 0.01 ion (100 eV) $^{-1}$.

In 6 M HNO₃, e_{aq}^- and H are converted into NO₂ and then into HNO₂, and the latter reacts with hydrogen peroxide. The OH

radicals react with NO_3^- and HNO_3 to give NO_3 radicals. The latter oxidise Ce(III). The resulting Ce(IV) enters into the reactions with HNO_2 and Bk(III). After that, the reduction of Bk(IV) and its transfer into the organic phase compete with each other. Since the potential of the Bk(IV)/Bk(III) pair decreases, Bk(IV) does not react with HNO_2 in the organic phase.

The stability of Bk(IV) in a solution of perchloric acid exposed to α -particles emitted by ^{244}Cm has been studied.¹⁸¹ According to our calculations, at $[\text{HClO}_4] = 1-5 \text{ M}$, the $G[-\text{Bk(IV)}]$ values vary from 4.2 to 5.1 ion $(100 \text{ eV})^{-1}$. At higher concentrations of the acid, the yields increase. As noted above, the theoretical yield for α -radiolysis in a 1–5 M solution of HClO_4 is 3.0 ion $(100 \text{ eV})^{-1}$. The higher values obtained experimentally are caused most probably by the presence of impurities introduced into the solution together with curium.

A study¹⁸² has been devoted to the behaviour of Bk(IV) in solutions of nitric acid under the action of β - and α -radiation (^{244}Cm was used as the source of α -radiation). The reduction of Bk(IV) was found to obey zero-order kinetics. Depending on the concentrations of HNO_3 and Bk(IV) and also on the dose rate, the $G[-\text{Bk(IV)}]$ values vary from 8.5 to 13.5 ion $(100 \text{ eV})^{-1}$. The theoretical value should be 4.5–5.5 ion $(100 \text{ eV})^{-1}$. Higher values are achieved due to the presence of impurities.

3. Solutions of californium ions

The formation of Cf(II) upon interaction of e_{aq}^- with Cf(III) in a deaerated solution of californium(III) containing *tert*-butyl alcohol (pH 5.1–5.3) has been detected by pulse radiolysis.³³ The rate constant measured in this study is presented in Table 3. It was found that Cf(II) is responsible for an absorption band with a maximum at 270 nm (the molar extinction coefficient at this wavelength is equal to $50 \text{ m}^2 \text{ mol}^{-1}$). The consumption of Cf(II) occurs according to first-order kinetics with a rate constant of $7 \times 10^4 \text{ s}^{-1}$. In solutions saturated with N_2O , the formation of Cf(IV) was not detected.

Two studies have been devoted to the reduction of $^{249}\text{Cf(IV)}$, bound into a complex with $\text{P}_2\text{W}_{17}\text{O}_{61}^{10-}$ induced by its own α -radiation in the presence of $\text{S}_2\text{O}_8^{2-}$ (see Ref. 1). At the beginning of the process [before ~50% of Cf(IV) is reduced], its rate does not depend on the concentration of Cf(IV), *i.e.* the reaction has the zero order; then the rate decreases and starts to depend on [Cf(IV)]. Calculation of $G[-\text{Cf(IV)}]$ based on the results of these studies leads to a value of 32.8 ion $(100 \text{ eV})^{-1}$. Evidently, this high yield is due to impurities.

It has been found¹⁷⁵ that Cf(IV) bound into a complex with $\text{P}_2\text{W}_{17}\text{O}_{61}^{10-}$ is reduced in α -radiolysis, the reduction yield being 7.5–31 ion $(100 \text{ eV})^{-1}$ in the pH range of 2.5–6.1 and at a concentration of the phosphotungstate of 0 to $6.1 \times 10^{-3} \text{ mol litre}^{-1}$. The high yields are apparently due to the presence of impurities.

IX. Conclusion

The above consideration indicates that substantial progress has been achieved in the chemistry of aqueous solutions of actinides. Radiolytic transformations of uranium, neptunium, plutonium and americium ions induced by γ - or α -radiation in aqueous solutions under various conditions have been studied in detail; in many cases, the mechanisms of these transformations have been identified. Interesting data about the influence of ionising radiation on aqueous solutions of berkelium ions have been obtained. The first results on the radiolysis of solutions of californium are available. The rate constants for many reactions between actinide ions and the primary products of radiation-induced decomposition of water and with inorganic free radicals (SO_4^- , NO_3 , CO_3^- , *etc.*) have been measured using the method of pulse radiolysis. Short-lived intermediates of a number of redox reactions of actinide ions in irradiated aqueous solutions have been identified and studied. A procedure for radiation-induced synthesis of heptavalent neptunium, plutonium and americium has been developed.

However, there are problems to be solved in this field of radiation chemistry. Some of them are formulated below. Note that this list is incomplete, but it points to possible lines of subsequent research in this practically important field of science.

Firstly, radiolysis of aqueous solutions of actinides in nitric acid still remains little investigated. This is mainly due to the fact that radiolytic transformations of nitric acid itself are not completely clear. The foregoing can be illustrated, for example, by the fact that the published values for the molar extinction coefficient of the NO_3 radical, which is among the major intermediate species in the radiolysis of this acid, differ by factors of 4–5 (see, for example, Refs 78 and 183).

Secondly, actinide ions undergo radiolytic transformations induced by their own α -radiation. However, no data about the yields of hydrated electrons in α -radiolysis can be found in the literature, which hampers in some cases interpretation of the results obtained.

Thirdly, the reactivity of actinide ions towards organic free radicals has not been adequately studied. This information would be especially important for describing and predicting the radiolytic behaviour of these ions, for example, in extraction systems used to process irradiated nuclear fuel.

Fourthly, additional investigations of the radiolytic transformations of actinide ions in biphasic systems are needed. This would be of interest for the technologies of separation and isolation of radionuclides from industrial solutions.

Fifthly, radiolysis of alkaline aqueous solutions of actinides has been studied only recently. The corresponding studies are of interest in view of the target-directed disposal of highly radioactive alkaline wastes stored in some nuclear centres. In this connection, it should be specially emphasised that it would be expedient to study the influence of ionising radiation on the solubility of plutonium hydroxides in alkaline solutions.

Finally, the problem of the influence of organic impurities on the radiolysis of aqueous solutions of actinides still remains acute. This refers, first of all, to the use of curium as an internal source of radiation. We repeatedly mentioned in the review that the presence of such impurities leads to increased radiation yields. Therefore, development of special methods for the purification of the samples of α -emitters prior to their introduction into solutions and employment of the external irradiation technique (for example, as was done in the 50–60s for the radiolysis of aqueous solutions under the action of α -particles emitted by ^{210}Po) are urgent tasks.

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^b — *Radiochemistry (Engl. Transl.)*

^c — *Dokl. Chem. Tech., Dokl. Chem. (Engl. Transl.)*

^d — *Russ. Chem. Bull. (Engl. Transl.)*

^e — *Russ. J. Phys. Chem. (Engl. Transl.)*

Advances in the methods of synthesis of organic compounds of mercury

V I Boev, A I Moskalenko, A M Boev

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Abstract. New data on the methods of synthesis and practical applications of organic compounds of mercury are surveyed and treated systematically. The bibliography includes 180 references.

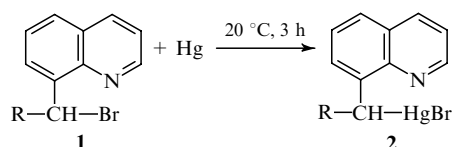
I. Introduction

The chemistry of organic compounds of mercury is one of the most extensive and thoroughly investigated fields of organometallic chemistry.^{1–7} Organomercury compounds (OMC) proved to be convenient objects for the solution of a series of fundamental problems of theoretical organic chemistry.^{8,9} They are also of practical importance, particularly in organic synthesis.^{3,7,10–12}

The original studies, published up to 1980, have been dealt with systematically in reviews^{4,5,9} and monographs,^{1–3,6–8} but during the last 15 years many new studies on the synthesis of OMC have been published. Certain data on particular aspects of the chemistry of OMC during the period indicated have been surveyed in reviews^{10–12} and dissertations.^{13–17} In the present review, a systematic and critical account is given of new and most significant, from our point of view, literature data on the methods of synthesis and applications of OMC.

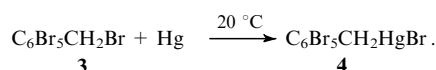
II. Insertion of a mercury atom in a C–Hal bond

The method of synthesis of OMC by the insertion of a Hg atom in a C–Hal bond was historically the first employed,¹ but it has still not lost its importance because of the availability of the initial reactants and the relative simplicity of the preparative use of the reaction. Thus the interaction of 8-(1-bromoalkyl)quinolines **1** with metallic mercury afforded¹⁸ the corresponding bromomercurioquinoline derivatives **2**, which are convenient models for the study of mechanisms of the S_E1-N type.^{8,18}



R = H, Me.

The reactions of hexahalotoluenes with metallic mercury have been investigated.^{19,20} Thus the interaction of pentabromobenzyl bromide (**3**) with mercury in benzene results in the formation of pentabromobenzylmercury bromide (**4**).



On the other hand, pentachlorobenzyl chloride **5** does not react with mercury under these conditions [when the reaction mixture is irradiated with UV light, 1,2-bis(pentachlorophenyl)ethane is formed].

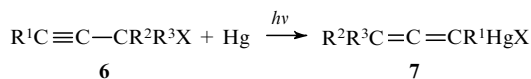
In the presence of a catalyst ($\text{Et}_4\text{N}^+\text{Br}^-$, $\text{Et}_4\text{N}^+\text{I}^-$, or NaBr), the bromide **3** and the chloride **5** react with mercury to form symmetrical OMC — bis(pentabromobenzyl)- and bis(pentachlorobenzyl)mercury. On UV irradiation, the latter decompose with liberation of mercury and the formation of 1,2-bis(pentachlorophenyl)ethanes (on irradiation with UV light for 2 h, compound **4** does not change). The influence of reaction conditions (solubility, the presence of a catalyst and atmospheric oxygen, illumination) on the composition and yield of the products of the interaction of the halogenated benzyl halides **3** and **5** with metallic mercury has been studied.²⁰ The optimum method of synthesis of type **4** benzylmercury derivatives has been proposed (DMF, Br^- , darkness, absence of atmospheric oxygen, 20 °C).

The interaction of metallic mercury with propargyl halides **6** has been investigated.²¹ On ethyne–allene rearrangement in a sealed tube under a nitrogen atmosphere and in sunlight in the course of 2 h,⁸ the allenyl derivatives of mercury **7** are formed. Their structure has been confirmed by IR and NMR spectroscopic data.

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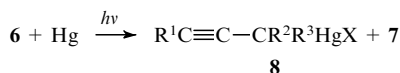
Uspekhi Khimii **66** (9) 874–900 (1997); translated by A K Grzybowski



$\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{H}, \text{X} = \text{I}; \text{R}^1 = \text{R}^3 = \text{H}, \text{R}^2 = \text{Me}, \text{X} = \text{I};$

$\text{R}^1 = \text{Ph}, \text{R}^2 = \text{Me}, \text{R}^3 = \text{H}, \text{X} = \text{I}; \text{R}^1 = \text{H}, \text{R}^2 = \text{R}^3 = \text{Me}, \text{X} = \text{Br}.$

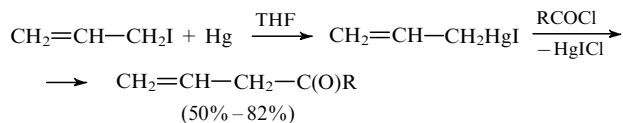
Other derivatives **6** form under these conditions a mixture of the corresponding propargylmercury derivatives **8** and the allenyl derivatives **7**.²¹



$\text{R}^1 = \text{Ph}, \text{R}^2 = \text{R}^3 = \text{H}, \text{X} = \text{Br}; \text{R}^1 = \text{Me}, \text{R}^2 = \text{R}^3 = \text{H}, \text{X} = \text{I};$

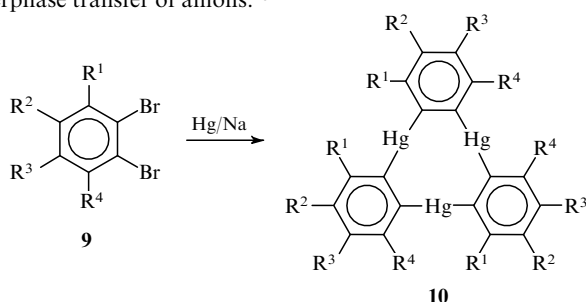
$\text{R}^1 = \text{Ph}, \text{R}^2 = \text{R}^3 = \text{H}, \text{X} = \text{I}; \text{R}^1 = (\text{CH}_2)_3\text{OAc}, \text{R}^2 = \text{R}^3 = \text{H}, \text{X} = \text{I}.$

The synthesis of allyl ketones, which proceeds *via* the formation of allylic OMC, has been described.^{22, 23}



$\text{R} = \text{Me}, \text{Ph}, 4\text{-ClC}_6\text{H}_4, 2\text{-FC}_6\text{H}_4.$

The substitution of a halogen by mercury is known³ to occur only on interaction of aryl halides with an alkali metal amalgam; the reaction with metallic mercury does not take place. The reactions of sodium amalgam with a series of aryl halides have been studied.²⁴ Thus the reaction of *o*-dibromobenzenes **9** with Hg/Na in THF for 2 h at 80 °C leads to *o*-arylenemercury trimers **10**, which are of preparative interest as crown-compounds for the interphase transfer of anions.²⁵

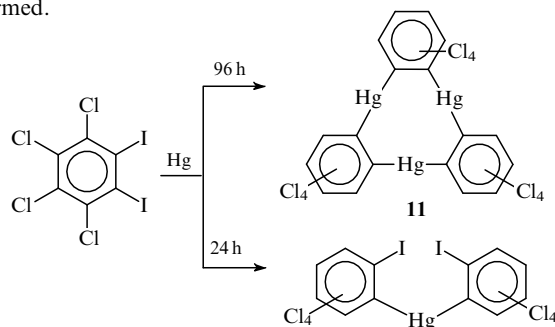


$\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{R}^4 = \text{H}; \text{R}^1 = \text{R}^3 = \text{R}^4 = \text{H}, \text{R}^2 = \text{Me};$

$\text{R}^1 = \text{Me}, \text{R}^2 = \text{R}^3 = \text{R}^4 = \text{H}; \text{R}^1 = \text{R}^4 = \text{H}, \text{R}^2 = \text{R}^3 = \text{Me};$

$\text{R}^1 = \text{R}^2 = \text{H}, \text{R}^3 = \text{R}^4 = \text{OMe}; \text{R}^1 = \text{R}^2 = \text{R}^3 = \text{R}^4 = \text{Me}.$

Compound **11** is formed as a result of the reaction of tetrachloro-1,2-diiodobenzene with mercury on heating (100 °C) in a sealed tube for four days.²⁴ When the reaction time is reduced to 24 h, only bis(3,4,5,6-tetrachloro-2-iodophenyl)mercury is formed.



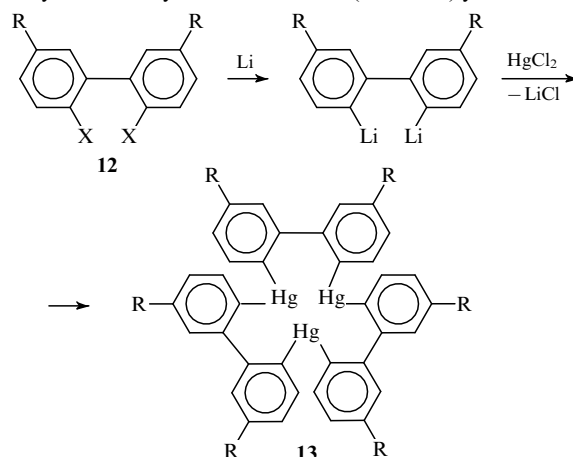
In conclusion of this section, one should note that, despite the long history of the use of reactions of the above types in syntheses of OMC, the mechanisms of these reactions have been scarcely studied.^{3–8} However, on the basis of the conditions (temperature, irradiation) under which mercury interacts with halogen-contain-

ing compounds, it is possible to make a choice in favour of a radical mechanism of the above reactions. Here the greatest activity is shown by iodides, while the bromo-derivatives react only when the carbon–bromine bond has been activated, for example by conjugation with a multiple bond,^{18–21} and chlorides are altogether inactive. Apparently, the limits of the applicability of the method of synthesis of OMC under consideration are determined primarily by the availability of the corresponding halo-derivatives and are not restricted by the choice of reaction conditions, which are standard in most cases.³

III. Substitution by mercury of other metal atoms and functional groups

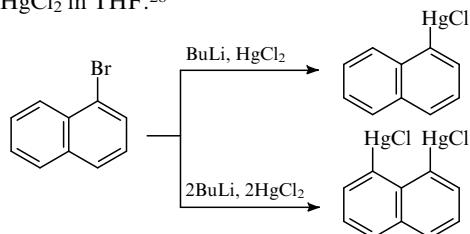
This approach to the synthesis of OMC is universal because it makes it possible, by varying the structures of the initial reactants, to synthesise in one stage a wide variety of mercury-containing substances with the required combinations of substituents at the mercury atom.

Thus bis(1-bicyclo[1.1.0]butyl)mercury has been obtained²⁶ in 75% yield by the reaction of the 1-lithiobicyclo-[1.1.0]butane–tetramethylethylenediamine (TMEDA) complex with mercury(II) chloride in THF. The reaction of substituted 2,2'-dihalobiphenyls **12** with lithium or butyllithium²⁴ and also of biphenylene with the Buli–TMEDA complex led to the synthesis²⁷ of the corresponding organolithium compounds, which on subsequent treatment with HgCl_2 in ether give rise to cyclic biphenylenemercury trimers **13** in low (2%–3%) yields.

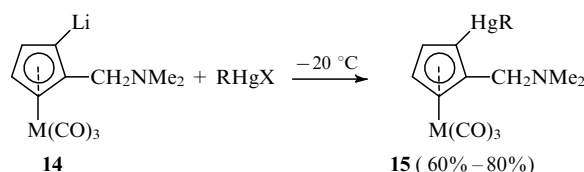


$\text{R} = \text{H}, \text{Me}, \text{Et}; \text{X} = \text{Cl}, \text{Br}.$

1-Naphthylmercury chloride and 1,8-di(chloromercurio)-naphthalene (depending on the molar reactant ratio) have been synthesised similarly by the reaction of 1-bromonaphthalene with butyllithium in a hexane–ether mixture with subsequent addition of HgCl_2 in THF.²⁸



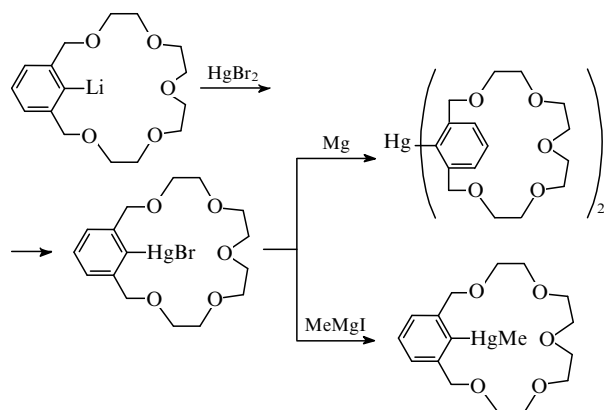
The optimum conditions have been found²⁹ for the reactions of lithium derivatives of (dimethylaminomethylcycloheptadienyl)tricarbonyl-manganese and -rhenium **14** with organic and metal carbonyl mercury salts, leading to the formation of symmetrical [$\text{R} = (\text{CO})_3\text{MC}_5\text{H}_3(\text{CH}_2\text{NMe}_2)$] and asymmetric ($\text{R} = \text{Cl}, \text{Br}$) OMC **15**.



M = Mn, Re; R = Cl, Br, (CO)₃MC₅H₃(CH₂NMe₂); X = Cl, Br.

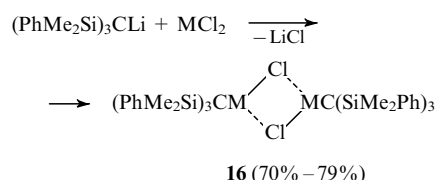
The lithium salts **14** have been synthesised *in situ* by the reaction of BuLi with the corresponding (dimethylaminomethyl)cyclopentadienyl)tricarboxymetal derivatives in THF at -70°C . Compounds **15** were characterised by ¹H and ¹³C NMR as well as IR spectroscopic data. Under these conditions, a downfield shift of the signals due to the CH₂ and Me groups in the ¹H NMR spectra relative to the signals of these groups in the initial complexes was observed. According to Suleimanov *et al.*,²⁹ the reason for this is the coordination of the nitrogen atom to the mercury atom, which has been confirmed by X-ray diffraction (XRD) study of the symmetrical OMC **15**. It was established that the length of the Hg–C bond (2.042 Å) is reduced compared with the statistical mean value 2.07 Å. The dimethylaminomethyl fragment has the conformation in which the lone pairs of the nitrogen atoms in the molecules of compound **15** are directed towards the mercury atom, but the Hg–N distance (2.933 Å) corresponds to only a weak secondary bond.

[2-(Bromomercurio)-1,3-xylylene]-18-crown-5 has been synthesised by the reaction of (2-lithio-1,3-xylylene)-18-crown-5 with HgBr₂ in THF and its reactions on treatment with magnesium and methylmagnesium iodide have been studied.³⁰



The existence of an intramolecular coordinate bond Hg···O with two out of the five oxygen atoms has been established by X-ray diffraction for all the OMC presented.³⁰ Similar reactions have been achieved with (2-lithio-1,3-xylylene)-15-crown-4.³⁰

The organosilicon compounds **16** have been obtained by the reaction of tris(dimethylphenylsilyl)methyl lithium with the chloride of the corresponding metal in an ether–THF mixture.³¹

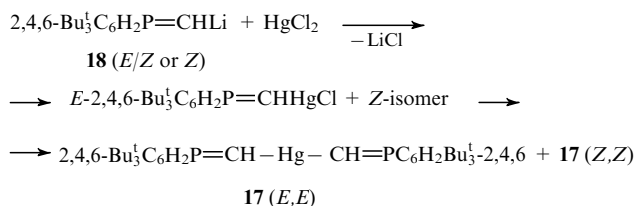


M = Zn, Cd, Hg.

The structures of the organometallic compounds obtained have been established by X-ray diffraction. They proved to be dimeric³¹ as a result of the formation of chloride bridges.

The phosphoalkenylmercurated compounds **17** in the form of the *E*- and *Z*-isomers have been synthesised in 30%–63% yields from the corresponding lithium salts **18** and mercury chloride in a hexane–THF mixture (Scheme 1).³²

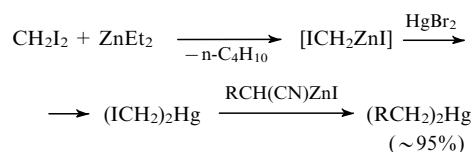
Scheme 1



It was established that the *Z*-isomers are thermodynamically more stable than the *E*-isomers, which are converted into the *Z*-isomers after a time.

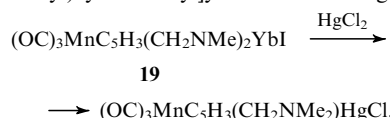
A laboratory method has been developed recently³³ for the synthesis of Bu₂Hg by the reaction of Bu^tMgCl with HgCl₂ in THF. The yield of bis(*tert*-butyl)mercury was then 73%.

A method has been proposed for the synthesis³⁴ of functionally substituted OMC involving the use of organozinc compounds¹⁸ *via* the intermediate formation of bis(iodo-methylene)mercury.



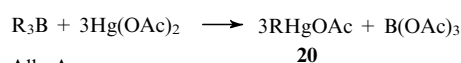
R = Buⁿ, cyclo-C₅H₁₁, PhCH₂, AcO(CH₂)₃, EtOCO(CH₂)₃, NC(CH₂)₃, Cl(CH₂)₄, Br(CH₂)₃P(O)(EtO)₂CH₂CH₂.

1-Chloromercurio-2-(dimethylaminomethyl)cymantrene has been obtained in 73% yield the reaction of [2-(dimethylaminomethyl)cymantrenyl]ytterbium iodide (**19**) or bis[2-(dimethylaminomethyl)cymantrenyl]ytterbium with HgCl₂ in THE.³⁵



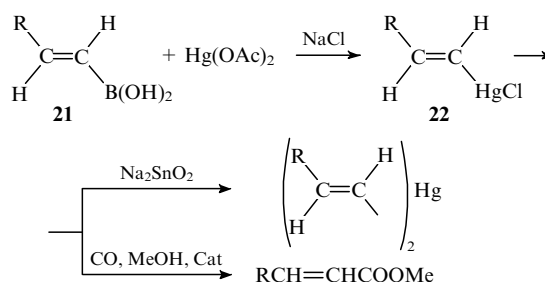
When mercury acetate is refluxed with tricarbonylcyclopentadienylmanganese in alcohol (molar reactant ratio 5:1), tricarbonyl[η⁵-pentakis(acetoxymercuro)cyclopentadienyl]manganese is formed.³⁶ It was subsequently used in the syntheses of a series of pentasubstituted derivatives of cymantrene.³⁶

Organylmercury acetates **20** are formed readily as a result of the transmetallation of organoboron compounds with mercury acetate.³⁷



R = Alk, Ar.

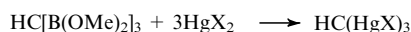
The interaction of the *E*-isomer **21** with mercury acetate in THF at room temperature and subsequent treatment with sodium chloride lead to the organomercurioalkenes **22** with retention of the configuration.³⁸ On treatment with an alkaline solution of Na₂SnO₂ in a THF–water mixture, the latter are readily symmetrised with formation of fully substituted mercurioalkenes having the *E*-configuration.³⁸



R = C₈H₁₇, Cl(CH₂)₃, I(CH₂)₃, AcO(CH₂)₈, PhO(CH₂)₃.

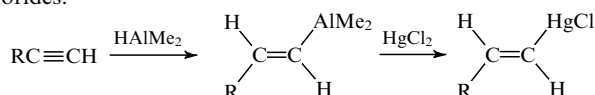
The reaction of compound **22** with CO and MeOH in the presence of a catalyst (Li_2PdCl_4 and MgO or Pr_2NEt) afforded a mixture of the *cis*- and *trans*-isomers of the corresponding unsaturated acid esters in 70%–80% yields.³⁹

Treatment of tris(dimethoxyboryl)methane with mercury salts in THF results in the substitution of the dimethoxyboryl groups by HgX with formation of trimercured methane.⁴⁰



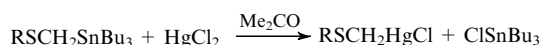
X = F, Cl, Br, OAc.

The interaction⁴¹ of terminal alkynes with organoaluminium hydrides in the presence of Cp_2ZrCl_2 proceeds regio- and stereo-selectively with formation of (*E*)-alkenylalanes, which react with HgCl_2 in THF to form the corresponding (*E*)-alkenylmercury chlorides.



R = C_8H_{17} , Ph, $\text{CH}_2=\text{CMe}$, C_6H_{13} .

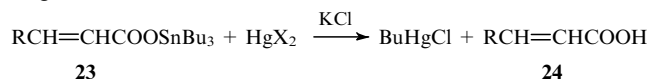
The exchange of tin for mercury as a result of the reaction



R = Me, Ph

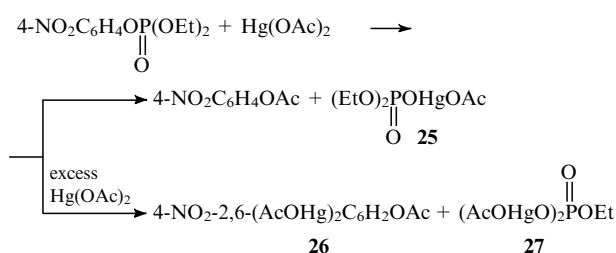
has been achieved.⁴² The yield of the reaction products is 90%.

It has been shown that⁴³ the demetallation reactions of the tributylstannyl derivatives of α,β -unsaturated carboxylic acids **23** on treatment with mercury salts proceed selectively with formation (after treatment of the reaction mixture with potassium chloride) of butylmercury chloride and the corresponding acids **24**. The mercuration of the double bonds was not observed in a single instance.

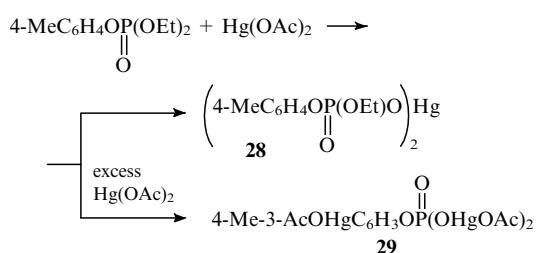


R = H, Me, Ph; X = Cl, OAc.

The interaction⁴⁴ of organophosphorus compounds with mercury acetate has been studied. The structure of the products formed depends on the reactant ratio and the reaction conditions. Thus the reaction of equimolar amounts of diethyl *p*-nitrophenyl phosphate and $\text{Hg}(\text{OAc})_2$ in hexane or toluene leads to *p*-nitrophenyl acetate and the mercury salt of the phosphate **25**.

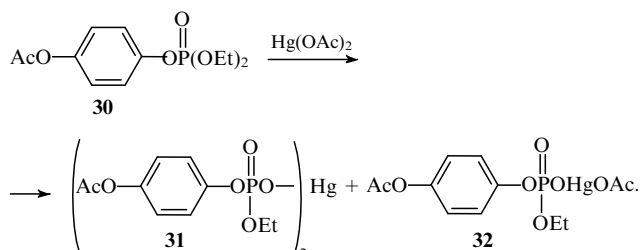


When the reaction is carried out in the presence of an excess of mercury acetate in acetic acid and on heating, compounds **26** and **27** are formed. The interaction of equimolar amounts of diethyl *p*-tolyl phosphate and mercury acetate leads to the salt **28**.⁴⁴

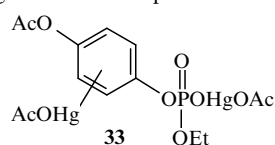


However, when an excess of the mercury salt is employed and the reaction is carried out in acetic acid, the product is compound **29**. The reaction of mercury acetate proceeds similarly also with other phosphates.⁴⁴

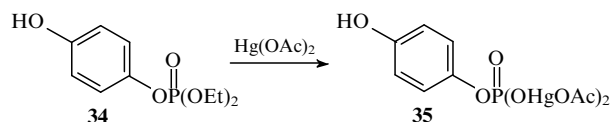
The interaction of equimolar amounts of compound **30** and mercury acetate at 20 °C affords a mixture of the products **31** and **32**.



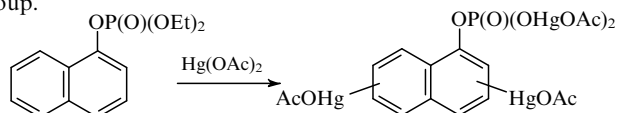
In the presence of an excess of mercury acetate, the product of mercuration in the aromatic ring, namely compound **33**, is formed together with compounds **31** and **32**.



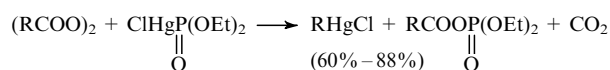
In the reaction of the phosphate **34** with mercury acetate, the only product is compound **35** regardless of the molar reactant ratio.



The interaction of α -naphthyl phosphate with mercury acetate leads to the mercuration of the aromatic ring and simultaneously to the substitution of the ethyl group by the mercurioacetate group.

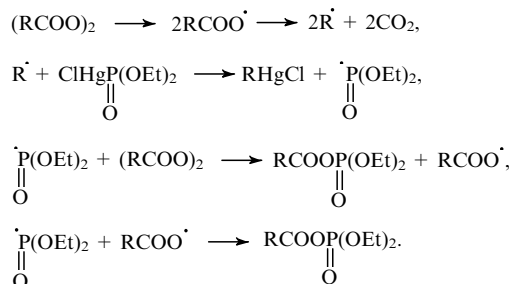


The synthesis of alkyl- and aryl-mercury chlorides by treating diethoxyphosphinylmercury chloride with acyl peroxides has been described.⁴⁵ The reaction is carried out in benzene with heating.



R = $\text{C}_{11}\text{H}_{23}$, $\text{C}_{15}\text{H}_{31}$, $\text{C}_{17}\text{H}_{35}$, Ph, 4- $\text{CH}_3\text{C}_6\text{H}_4$, 4- FC_6H_4 , 4- ClC_6H_4 .

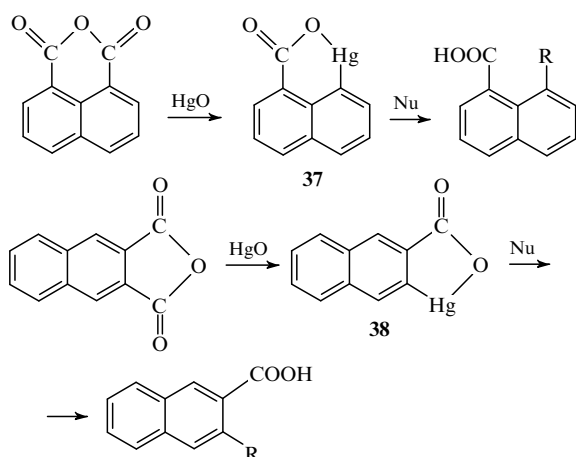
According to the authors,⁴⁵ the reaction proceeds *via* a radical mechanism.



The mechanism is confirmed by the fact that, in the reaction of *p*-toluyl peroxide with diethoxyphosphinylmercury chloride, a small amount of the mixed anhydride of *p*-toluic acid and diethyl phosphate, *p*- $\text{MeC}_6\text{H}_4\text{COOP}(\text{O})(\text{OEt})_2$ is formed.⁴⁵ The anhydride readily polymerises on distillation.

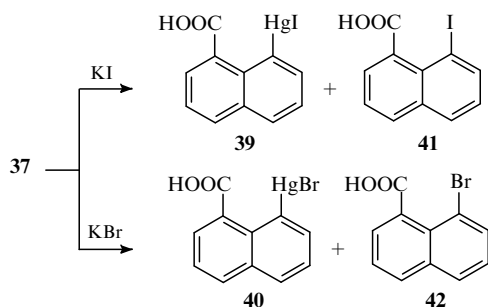
A convenient method has been developed⁴⁶ for the synthesis of bis(2,2,6,6-tetramethylpiperidin-4-yl)mercury (**36**) by the electrochemical reduction of 2,2,6,6-tetramethyl-4-oxopiperidine at a mercury cathode in a highly acid medium. Compound **36** is the starting reactant in the synthesis of the stable nitroxyl radical and bis(2,2,6,6-tetramethylpiperidin-4-yl-1-oxyl)mercury,⁴⁶ which is used as the mercury label in biochemical research involving the establishment of the structure of proteins.

Mercuration of the anhydrides of naphthalene-1,8- and naphthalene-2,3-dicarboxylic acids with HgO afforded respectively naphtho[1,8-*d,e*]-2,1-oxamercuracyclohexan-3-one (**37**) and naphtho[2,3-*d*]-2,1-oxamercuracyclopentan-3-one (**38**) respectively.⁴⁷ On interaction with nucleophiles (Nu), they give rise to the corresponding naphthalenecarboxylic acids — convenient synthons for the synthesis of various heterocyclic compounds.

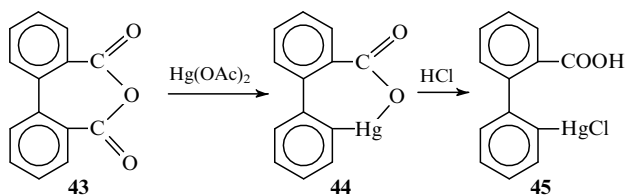


Nu = KI, H₂S, HCN; R = I, SH, CHO.

However, a reinvestigation⁴⁸ of the nucleophilic demercuration of compound **37** in aqueous acetic acid established that its interaction with potassium iodide or bromide leads to 8-iodo(-bromo)mercurionaphthoic acids **39** and **40** in 30% and 19% yields respectively) and to only traces of demercuration products — 8-iodo- and 8-bromo-naphthoic acids **41** and **42**.

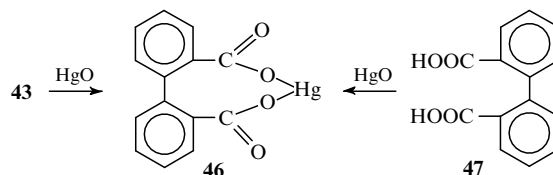


The mercuration product **44** is formed in the reaction of the anhydride of biphenyl-2,2'-dicarboxylic acid (**43**) with mercury acetate in the presence of NaOH. Its treatment with hydrogen chloride affords 2'-chloromercuriobiphenyl-2-carboxylic acid (**45**).⁴⁹

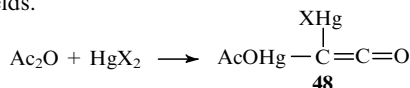


When compound **44** is treated with nucleophiles (KI, H₂S, HCN) in acetic acid, 2'-iodomercurio-, 2'-mercapto-, and 2'-formyl-biphenyl-2-carboxylic acids are formed.⁴⁹ The reaction

of the anhydride **43** with HgO in an aqueous solution of acetic acid is also described in the same communication. It is shown that the reaction product is the mercury salt of biphenyl-2,2'-dicarboxylic acid **46** (65% yield). This salt has also been obtained by the reaction of the dicarboxylic acid **47** with mercury oxide.⁴⁸



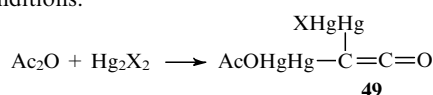
Interesting results have been obtained⁵⁰ on refluxing mercury salts HgX₂ with acetic anhydride in acetonitrile. The mercury derivatives of ketene **48** were then synthesised in 60%–80% yields.



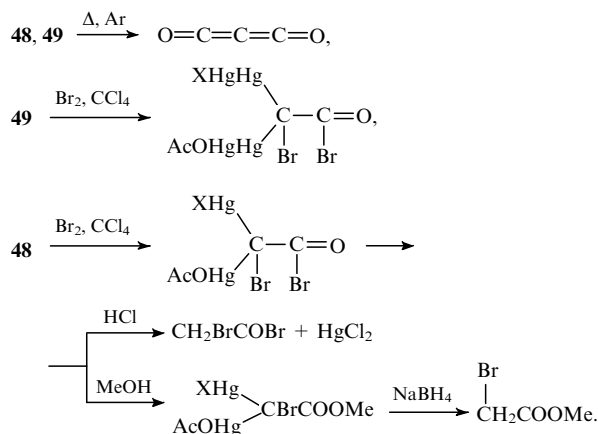
X = AcO, NO₃, ClO₄.

The reaction is accelerated in the presence of traces of sulfuric or perchloric acid. Compounds **48** are also formed when mercury salts HgX₂ are treated with ketene in acetonitrile at 20 °C.

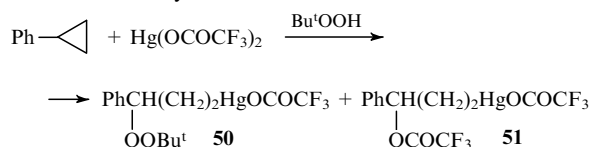
Stable organic derivatives of monovalent mercury **49** have been synthesised in 60%–80% yields by the reaction of monovalent mercury salts Hg₂X₂ with acetic anhydride under the same conditions.⁵⁰



On treatment with a dilute HCl solution, compounds **49** liberate Hg₂Cl₂ quantitatively, while the ketene derivative **48** dissolves in hydrochloric acid with formation of Hg²⁺ salts. When the mercurated ketenes **48** and **49** are treated with gaseous HCl in the absence of moisture, ketene and acetyl chloride are obtained.⁵⁰ The extensive synthetic possibilities of compounds **48** and **49** are demonstrated by the following reactions:⁵⁰



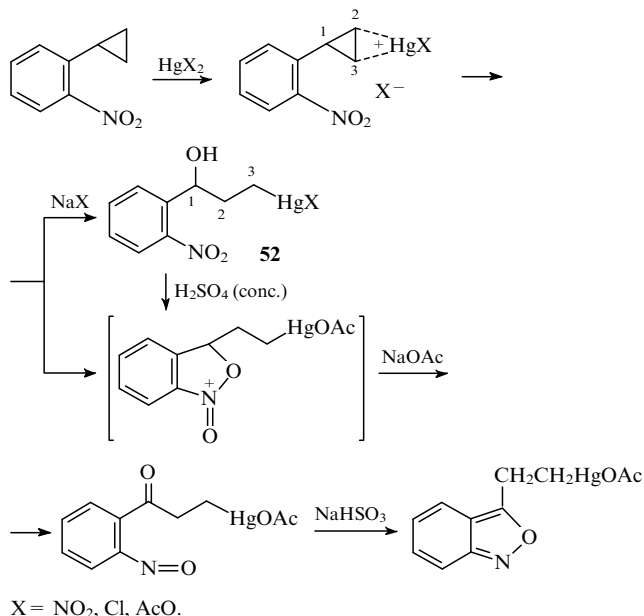
The reactions of various cyclopropane derivatives with mercury salts continue to attract the attention of investigators.^{51–57} Thus it has been shown that the interaction of phenylcyclopropane with a mixture of Bu^tOOH and mercury trifluoroacetate in methylene chloride at 20 °C leads to a mixture of the products **50** and **51** in an overall yield of 83%.⁵¹



When mercury acetate is used, the reaction does not occur.

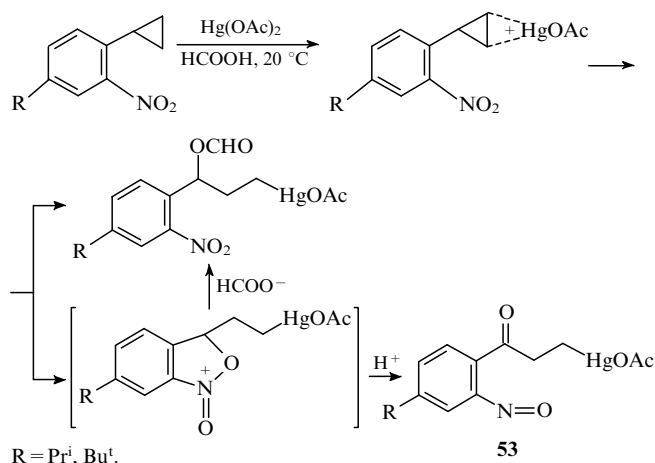
The interaction of cyclopropane with a mixture of mercury acetate and Bu^tOOH in the presence of HClO₄ (CH₂Cl₂, –40 °C, followed by 2 h at 20 °C) and subsequent treatment with KBr lead to a mixture of Bu^tOO(CH₂)₃HgBr, [BrHg(CH₂)₃]₂O, and AcO.(CH₂)₃HgBr, the structures of which have been established on the basis of ¹H, ¹³C, and ¹⁹⁹Hg NMR and IR spectroscopic data.⁵²

Successive interactions of *o*-nitrocyclopropylbenzene with mercury salts HgX₂ and further with saturated aqueous solutions of NaX led to the synthesis^{53,54} of the corresponding compounds **52**, which are of preparative interest^{54,55} for the synthesis of mercury-containing heterocyclic compounds.

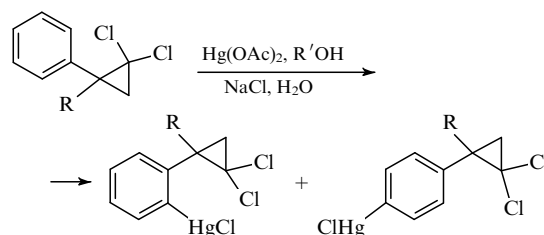


The mode of the conjugate mercuration of substituted *o*-nitrocyclopropylbenzenes by mercury acetate in formic acid depends on the nature of the substituents in the aromatic ring.⁵⁶ Under all the conditions investigated, the conjugate mercuration process is accompanied by the conversion of *o*-nitrocyclopropylbenzenes into mercurated *o*-nitrosopropiophenones **53** (Scheme 2).

Scheme 2

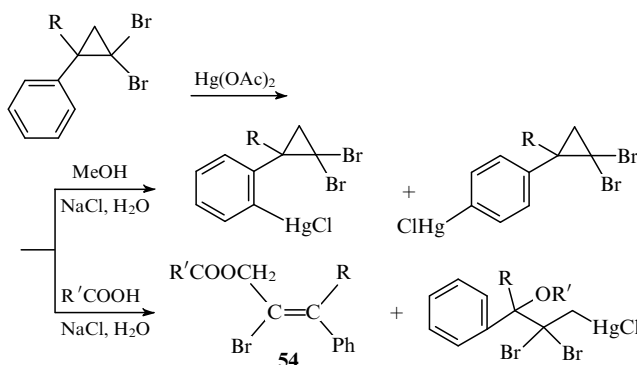


The behaviour of 1,1-dichloro- and 1,1-dibromo-2-phenylcyclopropanes in conjugate mercuration reactions has also been investigated.⁵⁷ It was established that, on treatment of 1,1-dichloro-2-phenyl- and 1,1-dichloro-2-methyl-2-phenylcyclopropanes with mercury acetate in hydroxylated solvents, the aromatic ring is mercurated in the *ortho*- and *para*-positions, while the three-membered ring is not involved.



R = H, Me; R' = Me, AcO, CHO.

1,1-Dibromo-2-phenylcyclopropane gives rise to an aromatic mercurio-derivative only in methanol.⁵⁷ In formic and acetic acids, the reactions of mercury acetate with 1,1-dibromo-2-phenyl- and 1,1-dibromo-2-methyl-2-phenylcyclopropanes proceed with the opening of the small ring. This process takes place stereo- and regio-specifically and leads to the alkenes **54** with the *Z*-configuration.



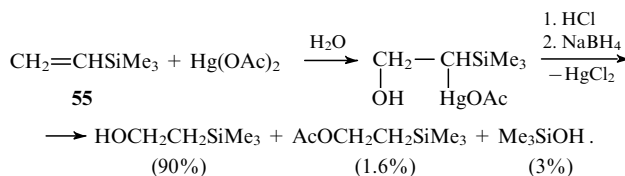
R = H, Me; R' = H, Me.

IV. Addition of mercury salts to a C = C bond

One of the most important and general methods for the formation of a carbon–mercury bond is mercuration,^{1–7} which can be regarded as electrophilic interaction of mercury-containing cations with electron-excess systems.

Among the methods for the synthesis of OMC, the reactions involving the addition of mercury salts to the multiple bonds in alkenes and ethynes in the presence of various nucleophiles are of special importance. An enormous number of mercury compounds, which possess a series of unique properties, have been synthesised by this method.^{3,6} These substances are remarkable because they exhibit strikingly a dual reactivity, like tautomeric compounds. In some cases, they react as true organometallic substances, whilst in others they behave like π -complex adducts of the mercury salt with an unsaturated compound as an addend, which can be substituted as a whole.³ Apparently, the vigorous development of methods of synthesis of OMC has continued because of these extremely interesting properties.⁷ During the last decade, attention has been concentrated on various aspects of the conjugate mercuration of unsaturated compounds.

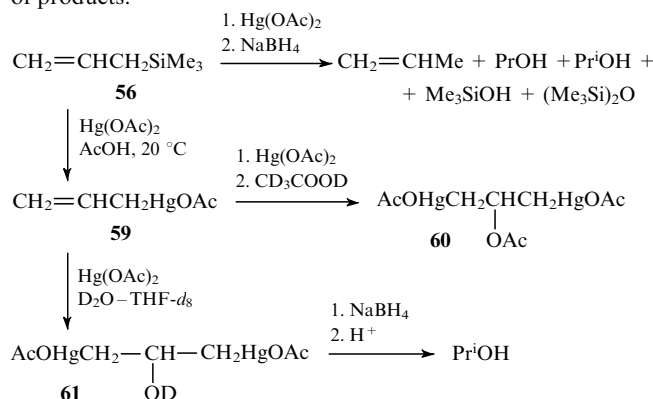
Thus the hydroxymercuration of silicon-containing alkenes — trimethyl-vinylsilane **55** and allyltrimethylsilane **56** — with mercury acetate in the 1:1 water–THF mixture has been studied.⁵⁸ The demercuration of the resulting hydroxymercuroacetate by the initial treatment with an alkaline solution of NaBH₄ and then with HCl leads to a complex mixture of reaction products.



The hydroxymercuration of the alkene **55** with mercury acetate in a D₂O-THF-*d*₈ mixture affords only 2-acetoxymercurio-1-deuterioxy-2-trimethylsilylthane (**57**) and, when CD₃COOD is used as the solvent, 2-acetoxymercurio-1-deuterio-2-acetoxy-2-trimethylsilylthane (**58**) is formed.⁵⁸

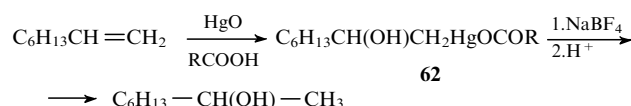


The hydroxymercuration of the allyl derivative **56** under the same conditions with subsequent demercuration of the resulting intermediate mercury-containing derivative also affords a mixture of products.⁵⁸



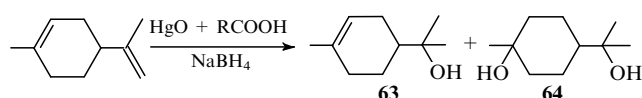
The interaction of the alkene **56** with mercury acetate in glacial acetic acid at room temperature leads to allyl mercurioacetate **59**, the reaction of which with Hg(OAc)₂ in CD₃COOD affords the demercurated compound **60**. The hydroxymercuration of compound **59** in a D₂O-THF-*d*₈ mixture leads only to the product **61**, which is converted into isopropyl alcohol on demercuration.⁵⁸

A method for the selective hydroxymercuration of alkenes by mercury salts, formed *in situ* from HgO and carboxylic acids under the influence of ultrasound, has been described.⁵⁹ Thus the interaction of oct-1-ene with HgO and RCOOH in proportions of 1 : 1 : 2 in aqueous THF leads to compound **62**, which affords a 85% yield of 2-octanol on reduction with NaBH₄.

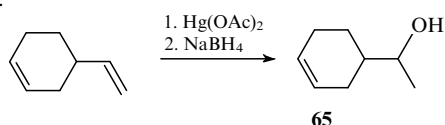


R = Me, Bu^t, C₉H₁₉, CBr₃, Pr, Ph.

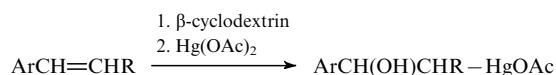
The hydroxymercuration of limonene leads, after reduction, to a mixture of the alcohols **63** and **64**, the ratio of which depends on the reaction conditions.⁵⁹



The highest yield (80%) of α-terpineol **63** is observed in Bu^tOH as the solvent, using C₁₇F₁₅COOH, and an exposure to ultrasound for 7 min. When the analogous reaction with 4-vinylcyclohexene was carried out in the presence of Hg(OAc)₂, the yield of 1-(cyclohex-3-enyl)ethanol (**65**) did not exceed 20%, while in the presence of PrCOOH and HgO with exposure to ultrasound for 2 h the yield of the alcohol **65** was 67% with 100% selectivity.⁵⁹



The biomimetic asymmetric hydroxymercuration of alkenes, catalysed by β-cyclodextrin, has been achieved.⁶⁰

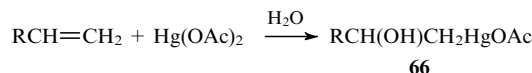


Ar = Ph, 4-MeC₆H₄, 4-ClC₆H₄;

R = H, CH₂OH, COOH, COOMe, COOEt, COOPrⁱ.

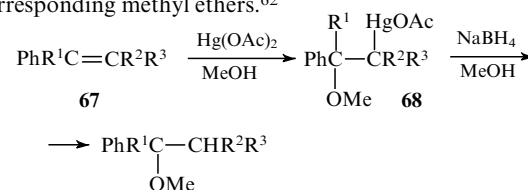
The asymmetric solvomercuration of alkenes has been carried out⁶¹ in chiral micellar systems with addition to the reaction mixture of the optically active salts PhCH(OH)·CHMeN⁺Me₂·C₁₂H₂₅Br⁻ or PhCH(OH)CHMeN⁺Me₂·C₁₆H₃₃Br⁻.

Compounds **66** were obtained as a result.



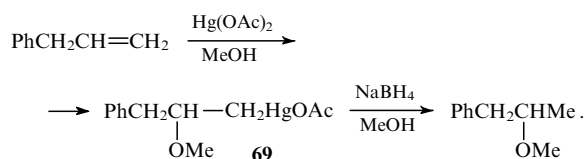
R = Ph, Buⁿ, Me(CH₂)₄CH(OH).

The interaction of styrene derivatives **67** with mercury acetate in methanol at 25 °C leads to the methoxymercuration products **68**, the reduction of which with NaBH₄ in MeOH gives rise to the corresponding methyl ethers.⁶²

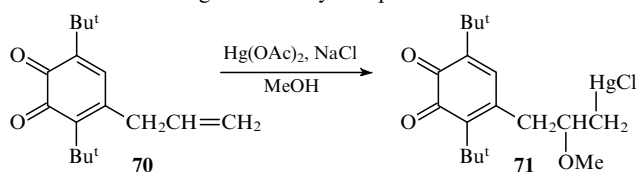


R¹, R², R³ = H, Me.

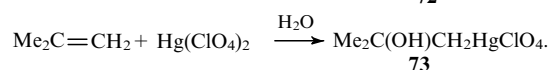
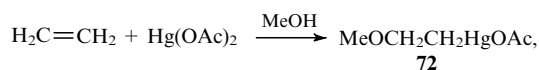
Allylbenzene reacts with mercury acetate under analogous conditions. subsequent demercuration of compound **69** leads to 2-methoxy-1-phenylpropane.⁶²



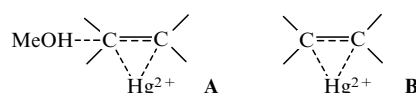
The presence of the allyl group in the molecule of the quinone **70** made it possible to carry out the conjugate mercuration reaction with mercury acetate in methanol,⁶³ which led to the formation of the organomercury compound **71**.



The mechanism of the mercuration of the C=C bond has been investigated⁶⁴ in relation to the methoxymercuration of ethene by mercury acetate in MeOH and the hydroxymercuration of 2-methylpropene by mercury perchlorate in water.

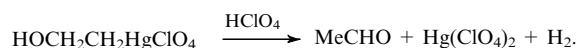


It was established that both reactions take place stereoselectively and that the addition of mercury to the C=C bonds proceeds *via* the formation of the intermediate **A** and its elimination proceeds *via* the intermediate **B**.



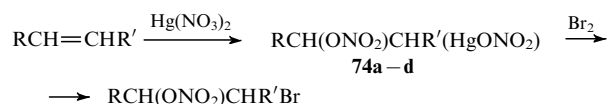
The protolysis of compound **72** is accompanied by the formation of the initial ethene, whilst the protolysis of

$\text{HOCH}_2\text{CH}_2\text{HgClO}_4$ is accompanied by hydride transfer with formation of acetaldehyde.⁶⁴

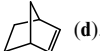


The protolysis of compound **73** in the presence of carboxylic acid salts leads to Bu^tOH .⁶⁴

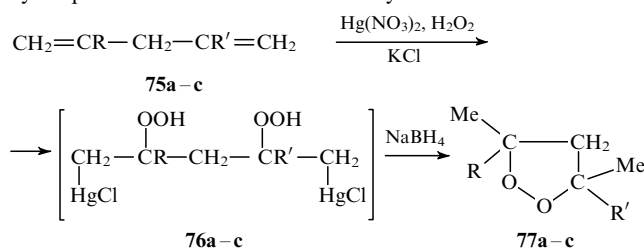
The nitratomercuration of a series of alkenes *via* the addition of mercury nitrate to the latter in methylene chloride at 0 °C has been achieved.⁶⁵ The reactions take place stereospecifically and, depending on the structures of the groups R and R', the *trans*- or *cis*-adducts **74a–c** are formed in ~100% yield. On treatment of the freshly prepared adducts **74** with bromine at 0 °C, HgNO_3 is substituted by the halogen.⁶⁵



R = Bu, R' = H (**a**); R = C_6H_{11} , R' = H (**b**); R = R' = Et (**c**);

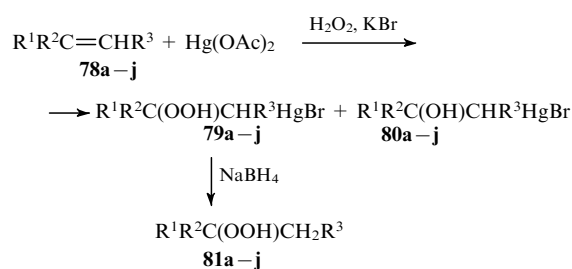
R, R' = ,  (**d**).

The interaction of nonconjugated dienes **75** with mercury nitrate and 80% hydrogen peroxide in CH_2Cl_2 at 20 °C followed by treatment with KCl or KBr leads to unstable mercurated hydroperoxides **76**, which are readily reduced by NaBH_4 to the cyclic peroxides **77a–c** in 64%–77% yields.⁶⁶



R = R' = H (**a**); R = R' = Me (**b**); R = H, R' = Me (**c**).

The monoalkenes **78a–j** interact with an equimolar amount of mercury acetate in 30% aqueous H_2O_2 and are converted on subsequent treatment with KBr into the mercurated hydroperoxides **79a–j** and the alcohols **80a–j**.^{67, 68}



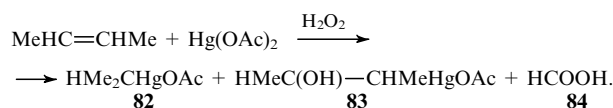
$\text{R}^2 = \text{R}^3 = \text{H}$: R¹ = Ph (**a**), 2-MeC₆H₄, (**b**), 4-MeC₆H₄, (**c**),

4-MeOC₆H₄, (**d**), Bu, (**e**);

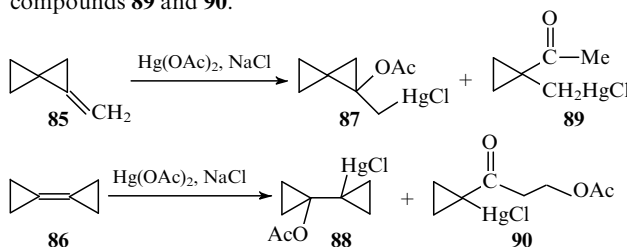
R¹ = Ph, R² = Me, R³ = H (**f**); R¹ = H, R² + R³ = (CH₂)₄ (**j**).

The yields of compounds **79** and **80** and their ratio depend on the nature of the alkene **78**. Thus the arylalkenes **78a–d** or the geminally substituted alkenes **78f** form only the corresponding hydroperoxides **79** in ~90% yield. Monoalkyl- or 1,2-dialkylalkenes afford mixtures of compounds **79** and **80** in low yields.⁶⁷ The reductive demercuration of compound **79** with sodium tetrahydroborate results in the formation of the alkylhydroperoxides **81a–j**⁶⁸ and not cyclic peroxides as in the case of compounds **77**. In contrast to the alkenes **78**, the interaction of

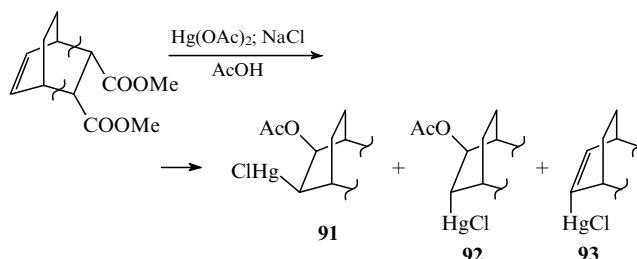
(*Z*)- or (*E*)-but-2-ene with $\text{Hg}(\text{OAc})_2$ in 30% H_2O_2 leads to the more complex mixture of reaction products **82–84**.⁶⁷



The reaction involving the acetoxymercuration of isomeric methylenecyclopropanes (methylenespiropentane **85** and bicyclopropylidene **86**) has been investigated.⁶⁹ The main reaction path is the formation of the adducts **87** and **88** respectively at the double bonds with retention of the three-membered ring. However, this is accompanied, albeit to only a slight extent, by the competitive addition to the C–C bond of cyclopropane with formation of compounds **89** and **90**.

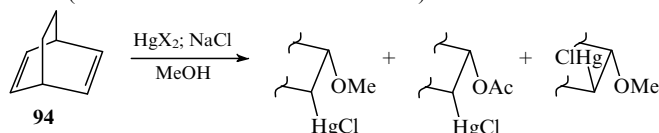


The stereoselectivity of the reaction of mercury acetate with dimethylbicyclo[2.2.2]oct-5-ene-2,3-*cis*-endo-dicarboxylate in acetic acid has been studied.⁷⁰ Several reaction products (compounds **91**, **92**, and **93**) were isolated in proportions of 11:4:5 respectively.



The formation of the unsaturated organomercury compound **93** in this reaction is due to the characteristic features of the structure of the intermediate, which in reactions of this type has the structure of a β -mercury-substituted carbonium ion.⁷⁰ The results obtained indicate severe steric requirements for the approach of the mercurating agent to the double bond of the initial compound while the coordination interaction of the carboxylate groups and the mercury atom plays a less significant role in this instance.⁷⁰

It has been established by ¹H, ¹³C, and ¹⁹⁹Hg NMR method⁷¹ that, in the interaction of mercury salts with bicyclo[2.2.2]octa-2,5-diene **94** in methanol, the main reaction path involves the formation of products with the *endo*-disposition of the mercury atom (the ratio of the adducts is 34:58:8).

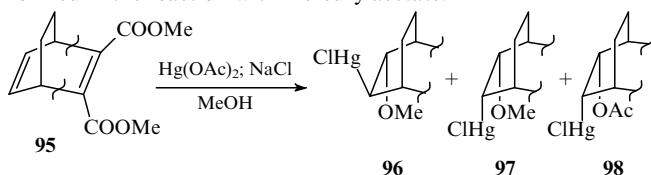


X = Cl, OAc.

The regioselectivity and stereospecificity of the reactions of mercury salts with dimethylbicyclo[2.2.2]octa-2,5-diene-2,3-dicarboxylate (**95**) in various solvents have also been investigated.⁷² The reagents employed were mercury acetate in MeOH or AcOH, mercury nitrate, and the $\text{Hg}(\text{OAc})_2\text{--NaN}_3$ (1:3) system in methanol. The products were isolated after treating the reaction mixture with an aqueous solution of NaCl.

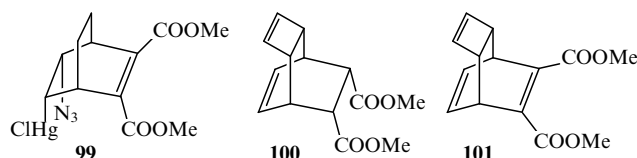
In contrast to the mercuration of the diene **94**,⁷¹ in the mercuration of the diene **95** with mercury acetate and nitrate in methanol the dominant path becomes the formation of the *trans*-solvatoadduct **96** with the *exo*-disposition of the Hg atom.⁷²

Compounds **96**, **97**, and **98** in proportions of 66:21:13 are formed in the reaction with mercury acetate.⁷²

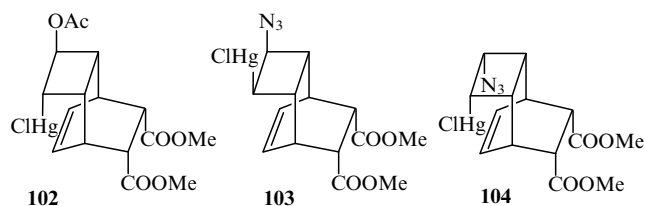


The use of mercury nitrate as the reactant leads to the solvatoadducts **96** and **97**, the content of compound **96** in the reaction mixture increasing to 77%.⁷² When the reaction with mercury acetate is carried out in AcOH or with the Hg(OAc)₂–NaN₃ system in methanol, the *endo*-products **98** and **99** are mainly formed in ~70% yield.

The regioselectivity and stereochemistry of the mercuration of the tricyclic diene **100** and triene **101** by a mixture of Hg(OAc)₂ and NaN₃ followed by the addition of NaCl to the reaction mixture have been investigated in a series of studies.^{73–81}

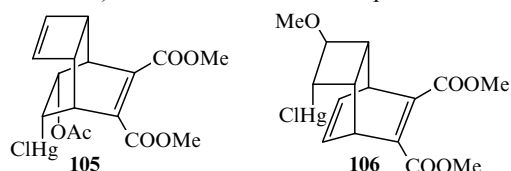


It was established that⁷³ the interaction of the diene **100** with mercury acetate in acetic acid results in the formation of the *trans*-solvatoadduct **102** with the *endo*-disposition of the mercury atom.

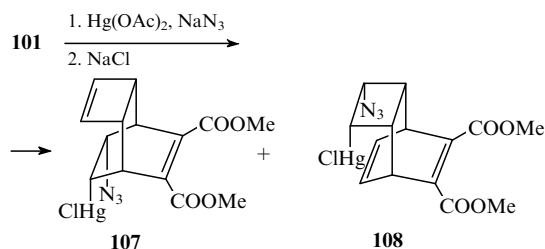


Different stereochemistry and regiochemistry were observed in the reaction of the diene **100** with the Hg(OAc)₂–NaN₃ mixture. Depending on the reactant ratio, only the *exo*-(*cis*-adduct) **103** (for the ratios 1:1:3) or a mixture of the *exo*-(*cis*-adduct) **103** and the *endo*-(*cis*-adduct) **104** (for the ratios 1:1:1) is formed,^{74–76} with the isomer **103** predominating.

When the reaction of the triene **101** is carried out in acetic acid, the mercury salt adds preferentially to the double bond of the cyclohexadiene fragment with formation of the *endo*-(*cis*-adduct) **105**. However, in methanol the double bond of the four-membered ring is involved in the reaction with mercury nitrate and *endo*-(*trans*-isomer) **106** is formed as the main product.^{77,78}

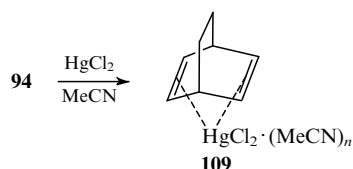


The study of the regiochemistry and stereochemistry of the azidomercuration of the triene **101** showed that the double bond of the cyclohexadiene fragment is involved preferentially in the reaction with formation of the *endo*-(*cis*-adduct) **107**; the attack on the four-membered ring proceeds from the sterically less accessible side and also involves the formation of the *endo*-(*cis*-isomer) **108**.⁷⁹



Such unusual regiochemistry in the conjugate mercuration of the diene **100** and the triene **101** may be due to the coordination interaction between the mercury salt and the sterically close double bonds⁸⁰ or, in more general terms, between the mercury salt and suitable functional groups of the substrate.⁸¹

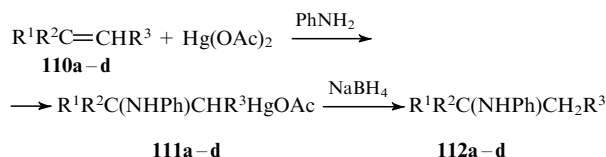
This has been recently confirmed by a study⁸² in which the possibility of the formation of a complex in the HgCl₂–bicyclo[2.2.2]octa-2,5-diene **94** system in acetonitrile was investigated by ¹⁹⁹Hg NMR. It was established that, for a series of solutions with a constant concentration of the mercury salt and a variable concentration of the diene, a pronounced downfield shift of the ¹⁹⁹Hg resonance signal is observed, which indicates the formation of a complex, probably having the structure **109**.



[94]/[HgCl ₂]	1.25	1.5	2.0	2.5	3.0	5.0
Δδ(¹⁹⁹ Hg) /ppm	11.88	14.85	18.20	21.80	25.61	43.56

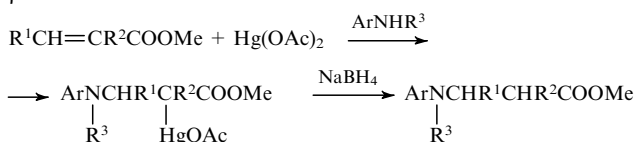
On the basis of the data obtained and using the conditions for the validity of the δ(¹⁹⁹Hg)^{–1}–[**94**] linear equation,^{83,84} the complex formation constant *K_f* and the relative chemical shift in the ¹⁹⁹Hg NMR spectrum for complex **109** were found by the method of least squares.⁸² These quantities proved to be 0.55–0.08 and 186±26 ppm respectively.

Apart from the azidomercuration reactions leading to the simultaneous formation of C–Hg and C–N bonds, aminomercuration, reactions, which result in the formation of bonds of the same type, have been described.^{85,86} The conditions for the direct amination of the alkenes **110a–d** by treatment with aniline and mercury acetate in an aqueous medium with the intermediate formation of the aminomercuration products **111a–d** have been elucidated.⁸⁵ Subsequent reduction of compounds **111** with NaBH₄ in an alkaline medium leads to the amines **112a–d**.



R¹ = R² = R³ = H (**a**); R¹ = Me, R² = R³ = H (**b**);
R¹ = R² = Me, R³ = H (**c**); R¹ = R² = R³ = Me (**d**).

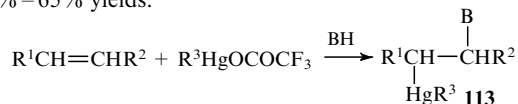
The reactions of the methyl esters of unsaturated acids with Hg(OAc)₂ and ArNHR led to the synthesis of the corresponding α-mercured esters, which were then reduced with NaBH₄ in an alkaline medium to the methyl esters of the corresponding β-aminoacids.⁸⁶



R¹ = R² = H; R¹ = R² = Me; Ar = Ph, 4-MeC₆H₄, 4-ClC₆H₄; R³ = H, Me.

Organomercury reagents, which had been rarely used previously^{3,6,7} for the conjugate mercuration of alkenes, have been employed for this purpose in recent years.^{87,88} Nevertheless, these reactions should be regarded as a convenient method of synthesis of asymmetric OMC.

The mercuration of styrene and cyclohexene by polyfluoroalkylmercury salts with participation of MeOH and HNMe₂ as nucleophiles has been investigated.⁸⁷ It was established that conjugate addition takes place in accordance with the Markovnikov rule with formation of the asymmetric OMC **113** in 24%–65% yields.



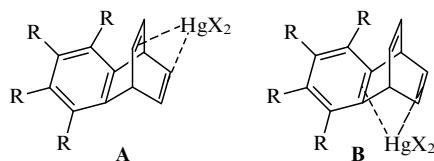
$R^1 = H$, $R^2 = Ph$; $R^1 + R^2 = (CH_2)_4$; $R^3 = CF_3$, C_3F_7 ; $B = OMe$, NMe_2 .

In the case of perfluoropropene in the presence of caesium fluoride in DMF, asymmetric fully substituted OMC with a perfluorinated substituent were obtained.⁸⁸



$R = Ph$, C_6Me_5 , $Ph_2C=CH$, 1,2,4,5-Me₄C₆HgOCOCF₃.

New aspects of the addition of mercury salts to a C=C double bond in various substrates have been investigated in a recently published series of studies.^{43,89–93} In particular, the regiochemistry and stereochemistry of the reaction involving the addition of mercury salts to benzobarrelene and tetrafluorobenzobarrelene in acetic acid and methanol have been investigated⁴³ and the influence of the structure of the substrate on the regiochemistry of the reaction has been examined. It follows from the data obtained⁴³ that the reaction products are formed as a result of the attack by the mercury salt on the double bond of the cyclohexadiene fragment both from the side of the arene ring and from the side of the bridging ethylene group. It is postulated here that the regiochemistry of the mercuration reaction is determined by the 'reagent–substrate' interaction and, in relation to the dienes indicated above, it may occur in two ways: the reagent–two double bonds of the cyclohexadiene fragments (**A**) and the reagent–double bond of the cyclohexadiene fragment–benzene ring (**B**).

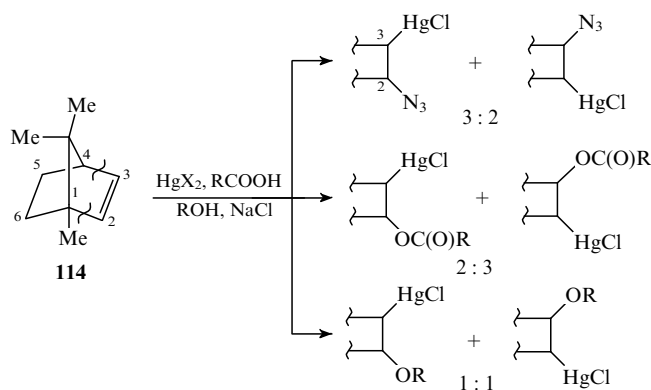


$R = H$, F ; $X = OAc$, N_3 .

According to the authors,⁴³ the preferential formation of the transition state **A** is characteristic of the reactions investigated. This suggests that the system of two skeletal double bonds exhibits more marked chelating properties relative to the mercury atom than the double bond–arene fragment system.

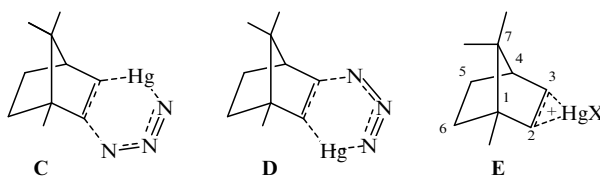
It has been established⁸⁹ that the regiochemistry of the mercuration reaction of bornylene **114** depends on the nature of the mercuring agent and the solvent.

It is important to note that the ratio of the regioisomeric adducts in the reaction of bornylene **114** with mercury azide is reversed when bornylene interacts with mercury acetate. According to Sokolova *et al.*,⁸⁹ this is due to the occurrence of the reactions *via* different mechanisms. The regiochemical data provide grounds for the hypothesis that mercury azide adds to bornylene **114** in accordance with a concerted mechanism *via* the transition states **C** and **D**. The transition state **C** is preferred in view of the smaller steric hindrance.



$X = OAc$, $OCOEt$, N_3 ; $R = Me$, Et .

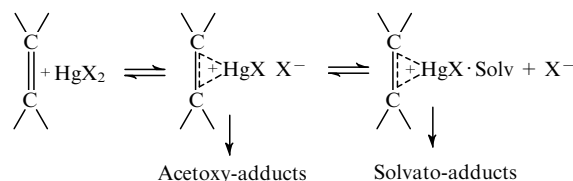
On the basis of the ratio of the regioisomers in the reaction of bornylene **114** with mercury acetate in alcohols and acetic acid, Sokolova *et al.*⁸⁹ suggested that the mercurenum intermediate **E** is formed in the reactions with mercury acetate and propionate and is then converted into the above reaction products.



$X = OAc$, $OCOEt$.

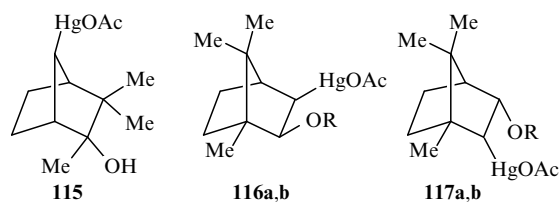
The preferential formation of the reaction products as a result of attack by the nucleophile on the 3-position, for which the steric factor is less important, is possible precisely for this mechanism.

The kinetics of the mercuration of bornylene⁹⁰ and cyclohexene⁹¹ have been investigated in various solvents (H_2O – $MeCN$, $MeOH$, $EtOH$, $PrOH$, $AcOH$) in the presence of sodium acetate and lithium perchlorate. The introduction of NaOAc into the mixture reduces sharply the rate of addition of mercury acetate to compound **114** and cyclohexene in alcohols. The formation of acetoxy-adducts then becomes the main path in the mercuration of compound **114** while the content of solvato-adducts falls from 76% (in the absence of NaOAc) to 19% (in 4×10^{-4} M NaOAc).⁹¹ A reaction mechanism with participation of ion pairs and a solvated mercurenum ion as intermediates has been proposed^{90,91} and confirmed by the method of stationary concentrations.



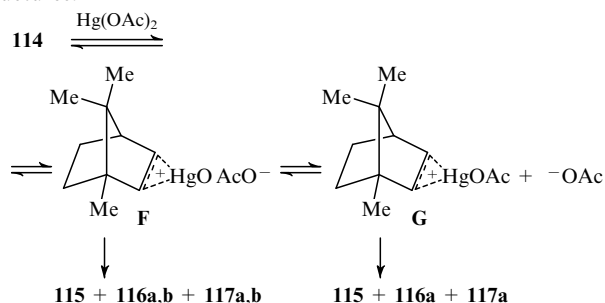
According to Kartashov *et al.*,⁹¹ the influence of NaOAc on the rate of formation of the reaction products is manifested *via* the common ion effect ($X = OAc$).

The reaction of mercury acetate with bornylene **114** has been investigated⁹² in the THF– H_2O and $MeCN$ – H_2O mixed solvents (75:25 by volume) and the influence of the addition of NaOAc on the rate of reaction and the composition of the products was studied. It was established that the addition of NaOAc to the $MeCN$ – H_2O mixture diminishes the amount of the rearranged product **115** and alters radically the ratio of the regioisomeric solvato-adducts **116a,b** and **117a,b**, stimulating the formation of the products of the addition of $Hg(OAc)_2$ to the bornylene double bond.

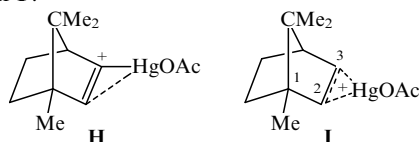


R = H (a), Ac (b).

It is believed⁹² that the reaction of mercury acetate with bornylene **114** proceeds with participation of the ion pair **F** and the free mercuronium ion **G**, but these intermediates have different structures.

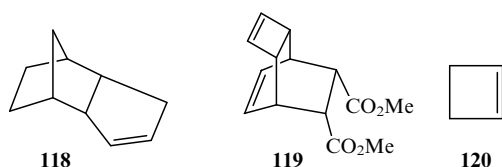


The considerable amount of the rearranged product **115** and the preferential formation of the solvato-adduct **116a** (in the absence of added NaOAc) give grounds for the assumption that the mercuronium ion **G** has the asymmetric structure **H**.⁹² When NaOAc is added, whereupon the reaction proceeds *via* the ion pair **F**, the preferential formation of the solvato-adduct **117a** and the appreciable inhibition of the Wagner–Meerwein rearrangement, leading to the product **115**, can apparently be explained by the more symmetrical structure of the cationic fragment **I** in the ion pair **F**.



The steric hindrance generated by the methyl group in the 1-position of the intermediate **I** to the approach of the nucleophile (OR) promotes the addition of the nucleophile ($-\text{OR}$) to the more accessible C(3) atom with the preferential formation of the product **117a**.⁹²

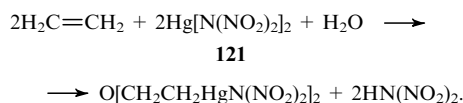
The kinetics of the addition of Hg(OAc)_2 to strained and unstrained alkenes have been investigated in MeOH in the presence of NaOAc.⁹³ The phenomenon of the salt effect led to the conclusion that, in the reactions with unstrained alkenes derived from allyl, cyclopentene, and cyclohexene, the reactant is the $^+\text{HgOAc}$ ion. In the case of strained alkenes such as compounds **118**–**120**, the reactant is Hg(OAc)_2 .



On the basis of these investigations, the mechanisms of the reaction involving the solvatomercuration of alkenes having different structures have been proposed.⁹³

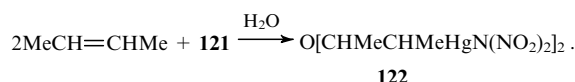
The reactions involving the addition of a new mercury salt — mercury dinitroamidate (MDNA) **121** — to alkenes such as ethene, propene, *cis*- and *trans*-but-2-enes, and norbornene have been studied recently.⁹⁴ In most cases, water, methanol, and diethyl ether were used as the solvent.

When ethene is passed into an aqueous MDNA solution for 5 h, the mercury-containing derivative of diethyl ether is precipitated in 51% yield.

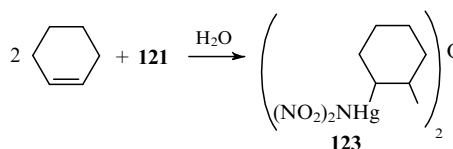


When an aqueous solution of MDNA is acted upon by propene, a product with an unknown structure, soluble in water and the usual organic solvents, is precipitated.

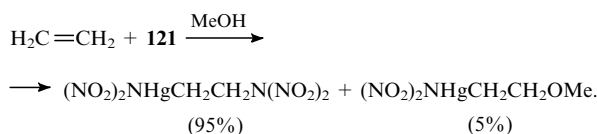
The addition of MDNA to *cis*- and *trans*-butenes in water leads, as in the case of ethene, to the corresponding dimercurated ethers **122** and, depending on the structure of the alkenes, different adducts are formed, which the authors⁹⁴ believe to be the *threo*- and *erythro*-isomers.



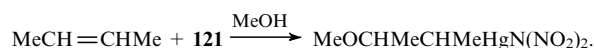
The product of the addition of MDNA to cyclohexene in water is also, according to IR spectroscopic data, a mercurio-derivative of the corresponding ether **123**.⁹⁴



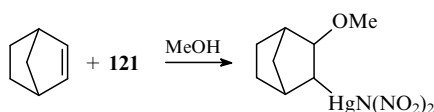
It was found that, when MeOH is used in the above reactions, the competition for the intermediate mercuronium cation is won not by $-\text{OMe}$ but by $-\text{N}(\text{NO}_2)_2$.⁹⁴ As a result, *N,N*-dinitro- β -dinitramidemercurioethylamine is formed in 95% yield and the product of the conjugate methoxymercuration — 1-methoxy-2-dinitramidemercurioethane is formed in only 5% yield as a result of the interaction of ethene with MDNA in methanol.



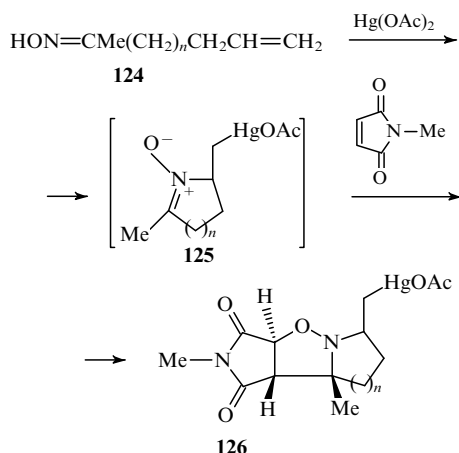
The conjugate mercuration involving the use of MDNA is extremely sensitive not only to the nature of the solvent but also to the structure of the alkene.⁹⁴ Thus the ratio of the products of the addition of MDNA to alkenes in methanol changes significantly on passing from ethene to its alkyl derivatives. According to ^1H NMR spectroscopic data, in the case of propenes the methoxymercuration products predominate over the corresponding *N,N*-dinitramidemercuration products, while in the case of but-2-enes only the methoxymercuration products are formed.



The addition of MDNA to norbornene in MeOH takes place with formation of only the methoxymercuration product having the *exo*-(*cis*-structure).⁹⁴

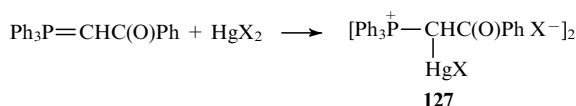


As a result of the addition of Hg(OAc)_2 to the double bond in the oximes **124** containing γ - or δ -alkenyl substituents, the intermediate compounds cyclize to the corresponding cyclic nitrones **125**. The latter react *in situ* with *N*-methylmaleimide (THF, 60 °C), forming the mercurated cyclic adducts **126** as a mixture of the *endo*- and *exo*-isomers.⁹⁵



$n = 1, 2$.

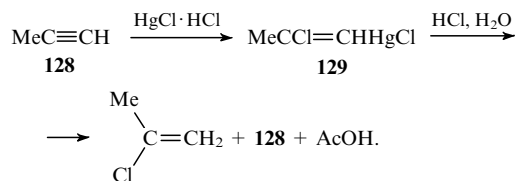
The addition of mercury salts HgX_2 to the $\text{C}=\text{P}$ double bond present in stable triphenylphosphonium ylides led to the formation of the corresponding salt-like adducts **127**, which are dimeric according to X-ray diffraction data.⁹⁶



$\text{X} = \text{Cl}, \text{I}$.

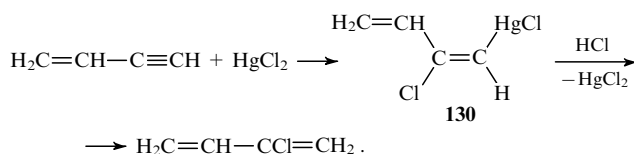
V. Addition of mercury salts to a $\text{C}\equiv\text{C}$ bond

This is one of the most general and universal methods of synthesis of unsaturated organomercury substances, which are of considerable scientific interest, for example for the study of stereochemical problems in organometallic chemistry.^{3,6} During the last 10–15 years, the studies on these lines have continued. Thus, the reaction of methylethyne **128** with the complex $\text{HgCl}_2 \cdot \text{HCl}$ has been investigated.⁹⁷ It was shown that the absorption of compound **128** at the freezing point of the $\text{H}_2\text{O}-\text{HCl}-\text{HgCl}_2$ system leads to (*E*)-1-chloromercurio-2-chloropropene **129**, which proved to be relatively unstable in air.



The reaction of compound **129** with a dilute hydrochloric acid solution leads to 2-chloropropene, the initial $\text{MeC}\equiv\text{CH}$, and acetic acid. The last compound is formed on hydration of $\text{MeC}\equiv\text{CH}$ formed from compound **129** as a result of β -elimination.

The interaction of mercury(II) chloride with vinylacetyne affords the *E*-1,2-adduct **130**.⁹⁷

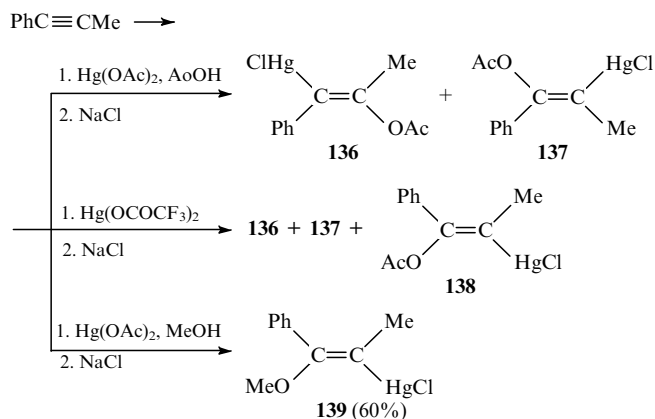


Compound **130** proved to be more stable than compound **129** during storage. However, on treatment with KI it decomposes with formation of the initial vinylacetyne while treatment with HCl converts it into 2-chlorobuta-1,3-diene.⁹⁷

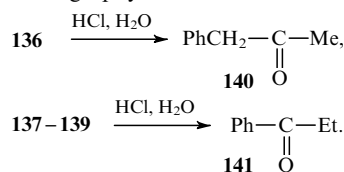
The conjugate alkoxymercuration of 2-methylbut-1-en-3-yne **131** by mercury acetate in various media has been studied.⁹⁸ A mixture of the products **132–134** is formed in alcohols, whilst in acid the sole product is compound **135** (Scheme 3).

The adducts **132–135** are readily reduced by NaBH_4 with formation of the corresponding unsaturated compounds.⁹⁸

The *E,Z*-stereochemistry of the addition of mercury salts to acetylenic hydrocarbons has been studied in a series of investigations.^{99–101} The reaction of methylphenylethyne with mercury acetate in acetic acid gives rise to a mixture of the isomers **136** and **137**, the reaction with mercury trifluoroacetate affords the three isomers **136–138** whilst that with $\text{Hg}(\text{OAc})_2$ in methanol results in the formation of only one product — (*Z*)-2-chloromercurio-1-methoxy-1-phenylprop-1-ene (**139**).⁹⁹

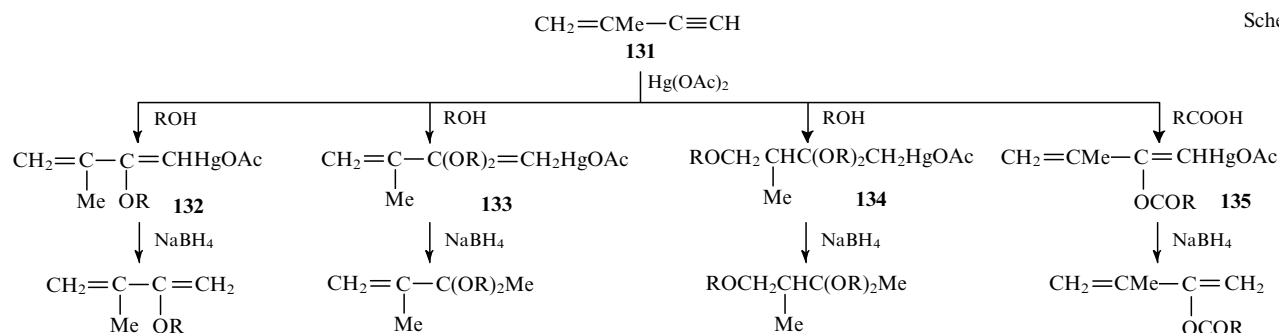


The protodemercuration of the alkene **136** in aqueous HCl solution yields the ketone **140**, whilst that of the alkenes **137–139** leads to the ketone **141**. The ketones were identified by gas–liquid chromatography.⁹⁹



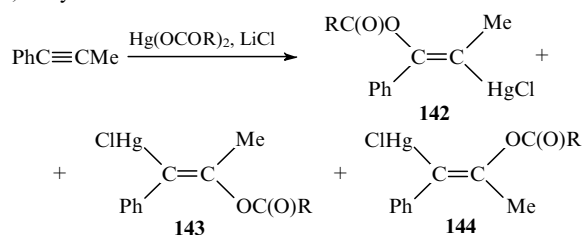
The study of the stereochemistry of the reaction of methylphenylethyne with $\text{Hg}(\text{OCOR})_2$ in acetic and propionic acids showed¹⁰⁰ that the composition of the reaction product is

Scheme 3



$\text{R} = \text{Me}, \text{Et}$.

determined by the reactant ratio. When the reactant ratio is 2 : 1 (with R = Me), only the *E*-isomers **142** and **143** are formed in proportions of 3 : 2. For a reactant ratio of 1 : 1, the *Z*-isomer **144** is formed in addition to the reaction products **142** and **143** (in proportions of 86 : 8 : 6). When the ratio of the initial reactants is 1 : 2, the yield of the *Z*-isomer **144** increases and reaches 15%.

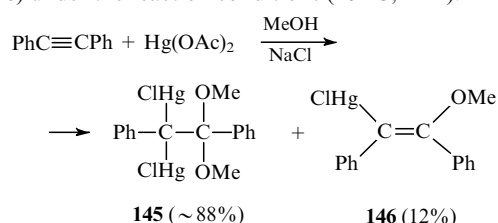


R = Me, Et.

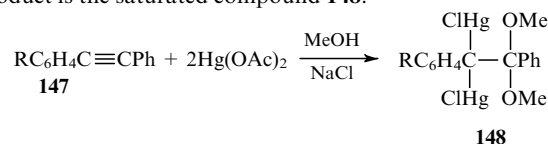
The reaction of diphenylethyne with mercury acetate in acetic acid leads only to the *E*-adduct $\text{ClHg}-\text{C}(\text{Ph})=\text{C}(\text{Ph})-\text{OAc}$.¹⁰¹

A study of the reactions of diphenylethyne with mercury salts in alcohols (R = Me, Et, Prⁱ) established^{102, 103} that mercury acetate reacts with diphenylethyne in methanol and ethanol to form the corresponding (β-alkoxyvinyl)mercurio-adducts as a mixture of the *Z*- and *E*-isomers. Mercury trifluoroacetate reacts with diphenylethyne in ethanol and propan-2-ol with a high degree of stereoselectivity, forming the *Z*-isomers, the structure of which has been established by X-ray diffraction.

Contrary to the data of Bassetti *et al.*,¹⁰³ Kartashov *et al.*¹⁰⁴ established that the main product of the reaction of mercury acetate with diphenylethyne in methanol is a compound which contains no double bond, namely 1,1-di(chloromercurio)-2,2-dimethoxy-1,2-diphenylethane (**145**), which can be partly converted into (*Z*)-1-chloromercurio-2-methoxy-1,2-diphenylethane (**146**) under the reaction conditions (20 °C, 24 h).

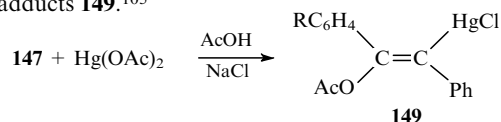


The reactions of arylphenylethyne **147** with mercury acetate in methanol and acetic acid have been studied.¹⁰⁵ The reaction in methanol has an unusual regiochemistry as a result of the addition of the electrophilic fragment $^+\text{HgOAc}$ to the carbon atom to which the substituted phenyl group is attached. The reaction product is the saturated compound **148**.



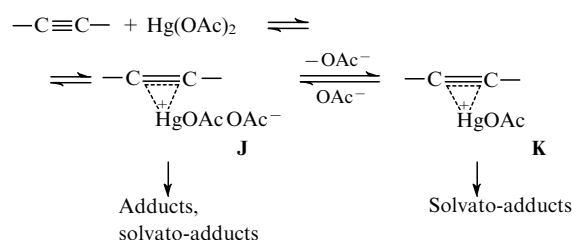
R = 4-Me, 4-OMe.

In acetic acid, the reaction proceeds with formation of the *E*-adducts **149**.¹⁰⁵



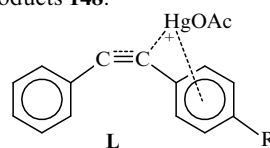
The kinetics of the reactions have also been investigated and the kinetic data have been analysed.¹⁰⁵ The influence of the addition of sodium acetate on the rate of formation and structure of the products **148** and **149** has been determined for the reaction in methanol. It was shown that the addition of NaOAc diminishes the rate of reaction, which becomes a minimum at a salt concentration of 3.0×10^{-3} M. For the reaction in acetic acid at the same

NaOAc concentration, no decrease in rate was observed.¹⁰⁵ This can probably be accounted for by the characteristic features of the methoxymercuration of acetylenic compounds for which we believe that the same general mechanism of conjugate mercuration is valid as for alkenes,^{91–93} examined in detail in the previous section.

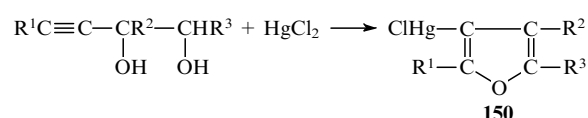


In acetic acid, the only intermediate is apparently the ion pair **J**, which dissociates in methanol to the anion ^-OAc and the cation **K**. In the case of the ion pair **J**, the triple bond is only slightly loosened and the positive charge is mainly concentrated on the mercury atom. In methanol, the ion pair **J** is converted into the cation **K** more rapidly than into the corresponding reaction products, but at the limiting sodium acetate concentrations the reaction probably proceeds preferentially *via* the ion pair **J** (as in acetic acid), which, being less reactive than the cation **K**, is converted more slowly into adducts and solvato-adducts.

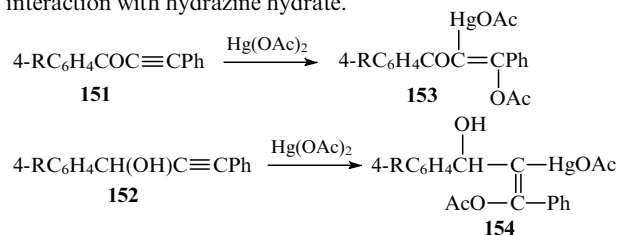
The unusual regiochemistry of compounds **148** can be explained by assuming that the free mercuronium ion **K** has an asymmetric structure, as in reactions with alkenes.⁹² In this case, a complex may be formed between the electrophilic fragment of the intermediate **L** and the benzene ring with its higher electron density, the π-complex being subsequently converted into the products **148**.¹⁰⁵



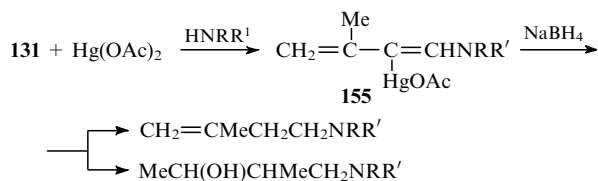
The interaction of equimolar amounts of 1,2-dialkylbut-3-yne-1,2-diols with mercury(II) chloride in alcohol leads to the corresponding derivatives of the mercurated furan **150** in high yields.¹⁰⁶



Other reactions of functionally substituted ethynes with mercury salts are also of interest. Thus the interaction of the ketones **151** or alcohols **152** containing a triple bond, with mercury acetate in acetic acid leads¹⁰⁷ only to the *E*-adducts **153** and **154**, which afford the corresponding 5-(4-R-phenyl)-3-phenylpyrazoles on interaction with hydrazine hydrate.



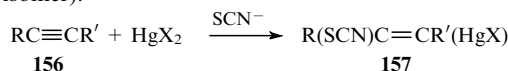
The addition of amines to compound **131** in the presence of mercury acetate has been investigated.¹⁰⁸ It has been suggested that the reaction results in conjugate aminomercuration of the enyne **131** with formation of conjugate organomercuriodienes **155**.



$\text{R} = \text{R}' = \text{Me}, \text{Et}; \text{R} + \text{R}' = (\text{CH}_2)_5, (\text{CH}_2)_2\text{O}(\text{CH}_2)_2.$

The demercuration of the adducts **155** with NaBH_4 in an alkaline medium leads to alkenylamines and aminoalcohols¹⁰⁸ which are difficult to obtain by other methods.

The thiocyanatomercuration products **157** have been obtained by the interaction of ethyne and its derivatives **156** with mercury salts HgX_2 in the presence of the thiocyanate anion.^{109,110} These compounds are formed regioselectively (in accordance with the Markovnikov rule) and stereospecifically (*E*-isomer).



$\text{R} = \text{R}' = \text{H}; \text{R} = \text{Bu}, \text{R}' = \text{H}; \text{R} = \text{OAc}, \text{R}' = \text{H}; \text{R} = \text{R}' = \text{Et};$

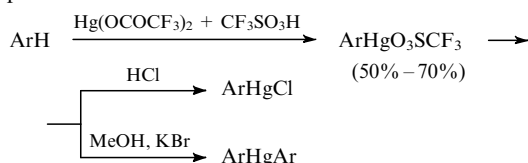
$\text{X} = \text{Cl}, \text{SCN}.$

The HgX group is readily substituted by hydrogen with retention of configuration on treatment of compound **157** with strong acids (H_2SO_4 , HBF_4) and NaBH_4 . It is also readily substituted by the halogens on treatment with iodine and bromine in pyridine or with CuCl_2 in acetonitrile.¹⁰⁹

VI. Mercuration of aromatic compounds

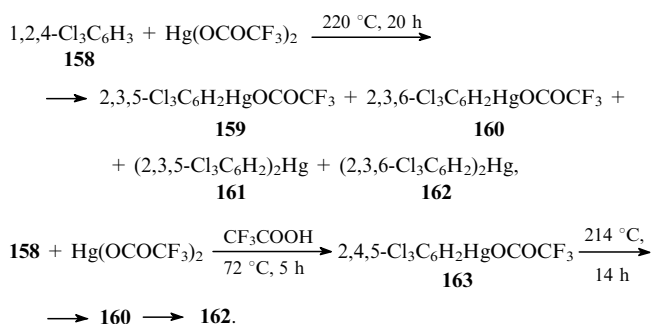
Many aromatic compounds (benzenoid and nonbenzenoid) are capable of entering into the mercuration reaction with divalent mercury salts, which leads to aryl-substituted OMC. The applicability of this reaction is very wide.

Many new examples of the mercuration reactions of aromatic compounds have been described during the last 15 years, which indicates that the studies on these lines are of current interest. Thus the mercuration of polyfluorobenzene derivatives with a mixture of mercury trifluoroacetate and fluorosulfonic acid in proportions of 1 : 2 has been achieved.¹¹¹



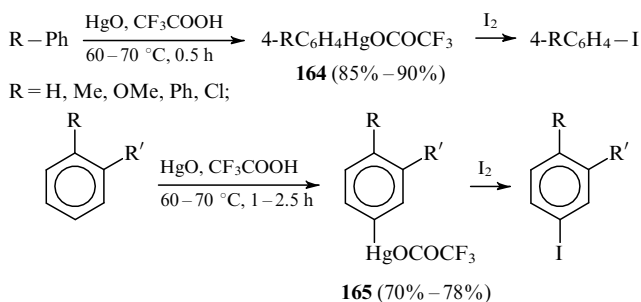
$\text{Ar} = \text{C}_6\text{F}_5, 4\text{-MeC}_6\text{F}_4, \text{C}_6\text{F}_4\text{H}, 3\text{-NO}_2\text{C}_6\text{F}_4, 3\text{-BrC}_6\text{F}_4, 4\text{-HOC}_6\text{F}_4, 4\text{-NH}_2\text{C}_6\text{F}_4, 3\text{-HOCC}_6\text{F}_4, 4\text{-MeOC}_6\text{F}_4.$

A mixture of organomercury polymers has been obtained by the mercuration of 1,2,4-trichlorobenzene (**158**) on heating with an excess of mercury trifluoroacetate. The individual OMC **159–162** were isolated from this mixture by extraction with benzene or xylene.¹¹²



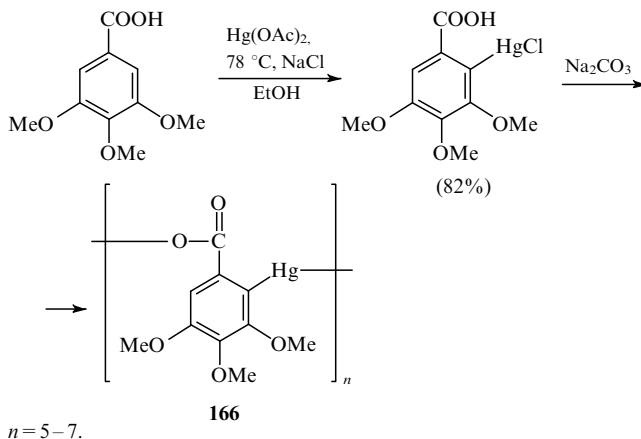
The position of the mercuritrifluoroacetate group in compounds **159–162** was determined by their reaction with iodine. Treatment of compound **158** with mercury trifluoroacetate while refluxing in CF_3COOH leads to a regiospecific reaction, which results in the formation of compound **163**. On refluxing in an excess of the chloride **158**, compound **163** isomerises to compound **160** with its subsequent symmetrisation to compound **162**.¹¹² The structures of the above OMC were demonstrated by their independent synthesis *via* organolithium compounds or by the Nesmeyanov reaction.¹¹²

Other benzene derivatives (with both electron-donating and electron-accepting substituents) are readily mercured on heating with a mixture of HgO and CF_3COOH forming the OMC **164** and **165**.¹¹³ The mercuration reaction then obeys the usual rules^{3,7} governing the direction of electrophilic substitution.



$\text{R} = \text{H}, \text{R}' = \text{COOH}; \text{R} = \text{Me}, \text{R}' = \text{COOH}; \text{R} = \text{Me}, \text{R}' = \text{Cl}.$

3,4,5-Trimethoxybenzoic acid is also comparatively readily mercured by mercury acetate with formation of 2-chloromercurio-3,4,5-trimethoxybenzoic acid, which is converted into the polymeric OMC **166** on treatment with sodium carbonate in acetone.¹¹⁴

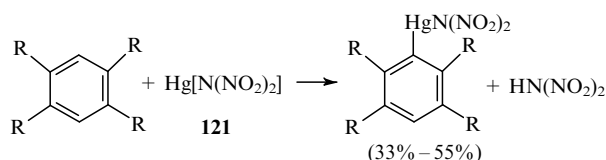


The interaction of benzene and its derivatives^{115,116} with a mixture of mercury oxide and trichloroacetic acid on heating (60–70 °C) leads to 90%–100% yields of the corresponding mercuration products:



$\text{Ar} = \text{Ph}, 4\text{-MeC}_6\text{H}_4.$

The mercuring capacity of mercury dinitroamidate **121** in relation to a series of aromatic compounds has been investigated.⁹⁴ It was established that benzene is not mercured by an ethereal solution of MDNA, since on prolonged refluxing of MDNA with benzene the decomposition of the mercury salt is faster than the mercuration reaction. However, refluxing of an aqueous solution of MDNA with benzene for 2 h leads to the product of monomercuration in the benzene ring (in 55% yield).⁹⁴ The more nucleophilic 1,2,4,5-tetramethylbenzene is readily mercured on refluxing in a methanol solution of MDNA. This reaction proceeds even in ether at room temperature.⁹⁴



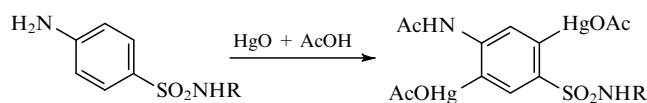
R = H, Me.

The mercuration of aniline in the *para*-position and of *N,N*-dimethylaniline with the aid of MDNA in alcoholic solution takes place very readily (in several minutes⁹⁴).



R = H, Me.

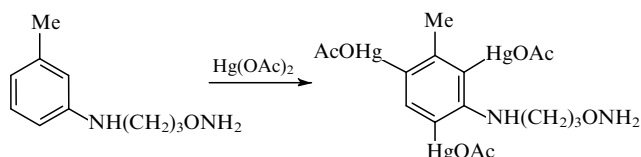
The mercuration of a large series of sulfanilamide preparations by heating them with HgO in acetic acid has been achieved.¹¹⁷ Dimercurated compounds were then obtained.



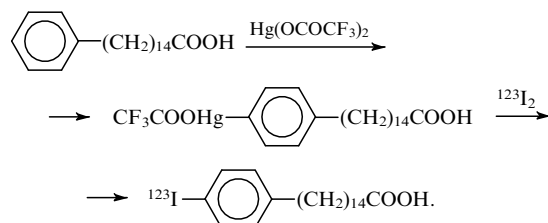
R = H, C(=NH)NH₂, , , .

3-Acetoxymercurio- and 3-chloromercurio-5-nitrosalicylaldehydes have been synthesised by mercurating 5-nitrosalicylaldehyde with mercury acetate.¹¹⁸ It has been suggested that these OMC be used for the simultaneous introduction of mercury and pH-sensitive functional groups into proteins which do not contain thiol groups in order to investigate their structure.¹¹⁸

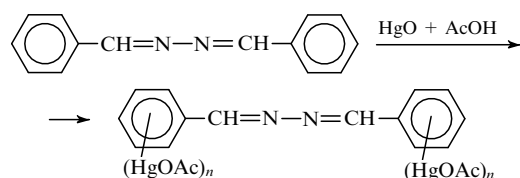
With the aim of synthesising mercury-containing reagents for the determination of carbonyl groups in biochemical research, *O*-substituted hydroxylamine, which makes it possible to introduce aminoxy-groups into proteins under mild conditions, was mercurated.¹¹⁹



In order to obtain radiopharmaceutical preparations labelled with radioactive iodine (¹²³I), 15-(4-iodophenyl)pentadecanoic acid was synthesised by mercurating 15-phenylpentadecanoic acid with mercury trifluoroacetate and subsequent treatment with radioactive iodine.¹²⁰

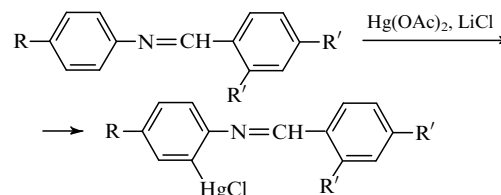


The mercuration of benzylideneazine with HgO in glacial acetic acid at 37–39 °C for 3 h leads to polymercured compounds which are insoluble in many solvents and decompose at 200 °C without melting.¹²¹



n = 2–5.

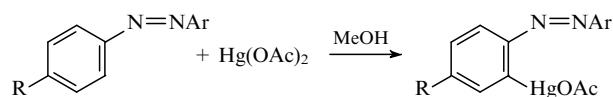
In contrast to this, arene azomethines interact with mercury acetate in alcohols (MeOH, EtOH) to form the corresponding products of *ortho*-mercuration in the *N*-substituted benzene ring in 80%–92% yields.¹²²



R = H, Me, OMe, Cl, Br, I; R' = OMe, NO₂.

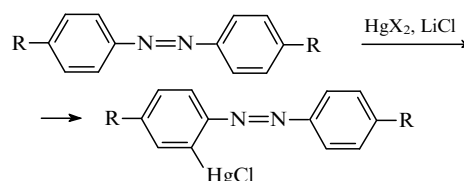
It follows from MINDO calculations of the regioselectivity of the mercuration of *N*-benzylideneaniline, *N*-benzylidene-2-toluidine, and 2-methoxy-*N*-(4-nitrobenzylidene)aniline that the electron density in the *N*-substituted benzene ring in the stable conformation is higher¹²³ and mercuration in this fragment takes place preferentially.¹²²

The mercuration of aromatic azo-compounds by mercury acetate or trifluoroacetate on refluxing in methanol leads only to monomercured compounds.^{124, 125}



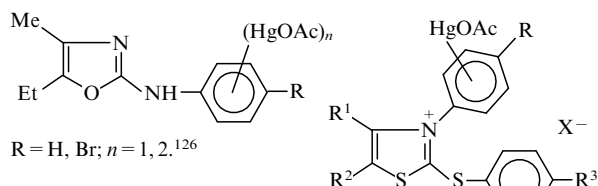
R = Me, NO₂, COOH;

Ar = 2,4-(HO)₂C₆H₃, 3,4,5-(HO)₃C₆H₂, α-C₁₀H₇, β-C₁₀H₇;



R = Bu, C₁₀H₂₁, OBu, OC₈H₁₇; X = OAc, OCOCF₃.

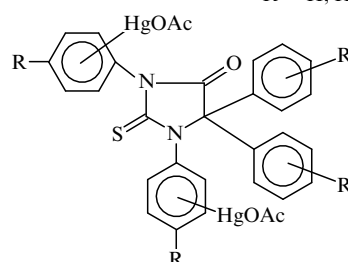
In order to enhance the fungicidal and bactericidal activities of potential pesticides, a series of heterocyclic compounds have been mercurated by mercury acetate in acetic acid.^{126–130} Mercury then substitutes a hydrogen atom in the benzene ring linked to the nitrogen atom of the heterocycle or to the nitrogen atom of the amino-group in the *para*- (if it is free) or *ortho*-position. Depending on the reactant ratio, mono- and di-mercurated derivatives are formed.



R = H, Br; n = 1, 2.¹²⁶

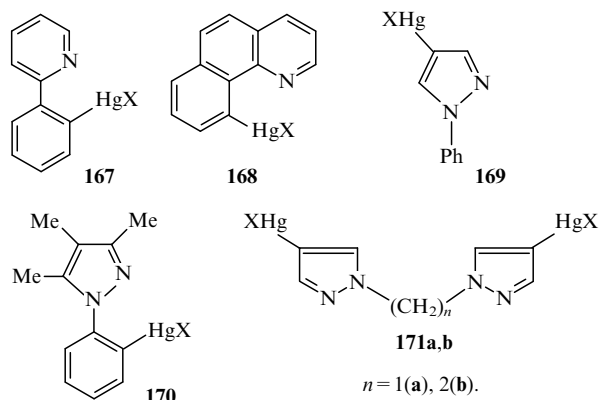
R¹ = Me, R² = Et; R¹ = R² = Me;

R³ = H, Hal, Me, OMe, NO₂, COOH.¹²⁷



R, R' = H, Alk, Hal, NO₂, COOH, OH, C₁₀H₇.^{128–130}

The mercuration of 2-phenylpyridine, benzo[*h*]quinoline, 1-phenylpyrazole, 3,4,5-trimethyl-1-phenylpyrazole, bis(pyrazol-1-yl)methane, and 1,2-[bis(pyrazol-1-yl)]ethane by mercury acetate in alcohol afforded the corresponding OMC **167**–**171a,b** in 50%–90% yield.^{131, 132}

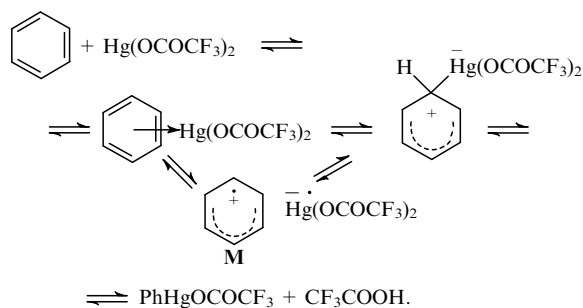


X = OAc, Cl.

It is difficult to deduce any kind of rules from the above data.^{131, 132} However, we may note that, as in previous studies,^{126–130} in the presence of aryl and heteroaryl fragments in the molecule, mercuration takes place in the benzene ring (regardless of the nature of the substituent in the latter) and does not involve the heterocyclic ring. Only in the absence of an activated benzene ring in the structure of the mercured compound does mercuration take place in the heterocycle (with formation of compounds **169** and **171a,b**). We may note that, as for the majority of pyrazoles entering into S_E reactions, the mode of substitution is determined predominantly by the pyridine nitrogen atom (this can be seen from the study of the mercuration products).

Comparison of the data in Refs 126–130 and in Refs 131 and 132 shows that in the case of compounds **167**, **168**, and **170** the formation of *para*-isomers is not observed at all, whereas Mahapatra and coworkers^{126–130} noted their predominant formation.

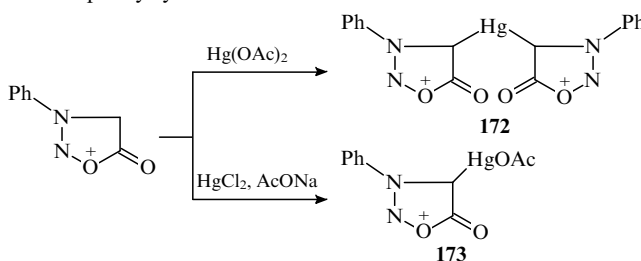
A special study by the EPR method demonstrated that, in the interaction of mercury trifluoroacetate with certain arenes (acenaphthene, anthracene, biphenyl, *p*-terphenyl, pyracene, hexahydopyracene, and triptycene) in trifluoroacetic acid, type **M** radical-ions are formed initially, which is followed by the effective mercuration of the arenes listed above. The following mechanism of the mercuration of benzenoid aromatic systems with the aid of mercury trifluoroacetate, which includes the generally known^{3, 7} stages involving the formation of π - and σ -complexes in the corresponding S_E reactions, has been proposed¹³³ on this basis.



Thus the data presented above have shown that aromatic electrophilic mercuration reactions can have, in principle, an oxidation-reduction stage. However, this conclusion is apparently valid only for the most reactive aromatic hydrocarbons¹³³ and electrophiles with sufficiently marked oxidising properties.

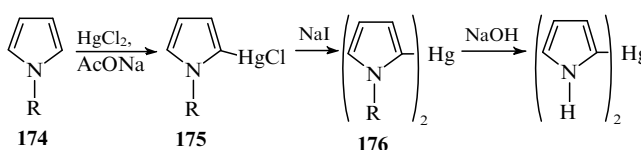
Heterocyclic compounds containing π -electron-excess systems are also readily mercured by mercury salts.³ In particular, 3-phenylsydnone is mercured by mercury(II) chloride or acetate in methanol.¹³⁴ Depending on the reaction conditions and the

reactant ratio, the fully substituted OMC **172** or 4-acetoxymercuro-3-phenylsydnone **173** are formed.



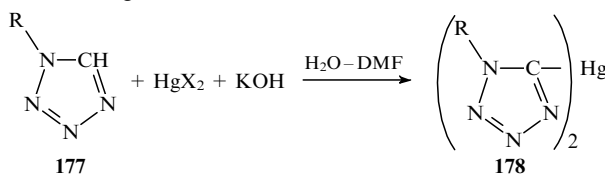
The sydnone **173** exhibits a high antibacterial activity against *Staphylococcus aureus* and *Escherichia coli*.¹³⁴

Under analogous conditions, the *N*-substituted pyrroles **174** are mercured in the 2-position.¹³⁵ The OMC **175** obtained are readily symmetrised on treatment with NaI in acetone with formation of the OMC **176**, which afford bis(pyrrol-2-yl)-mercury on interaction with alkali.



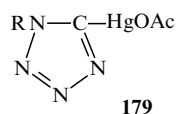
R = Ac, O₂SPh.

The 1-substituted tetrazoles **177** are smoothly mercured at room temperature by mercury salts in an alkaline medium at a ring carbon atom with formation of the symmetric C-mercuriotetrazoles **178** regardless of the reactant ratio.¹³⁶



R = Me, Ph; X = Br, I, AcO.

In neutral and acid media, the mercuration of the tetrazoles **177** takes place under more severe conditions with formation of either compounds **178** or the 5-acetoxymercuro-derivatives **179** depending on the reactant ratio.¹³⁶

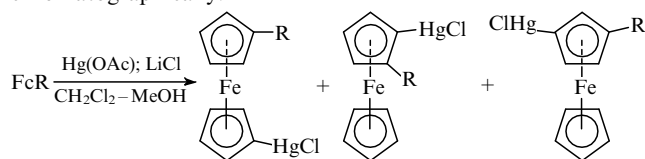


It is of interest that 2-substituted tetrazoles do not enter into similar reactions under the conditions described.¹³⁶

Being largely electron-deficient, six-membered π -electron heterocyclic compounds are mercured with difficulty under severe conditions. Thus the C-mercuration of 2,4-dimethoxypyrimidine by mercury acetate on refluxing in acetic acid with formation of 5-acetoxymercuro-2,4-dimethoxypyrimidine has been described.¹³⁷ Various methods for the direct C-mercuration of pyrimidine derivatives (uracil, 2-thiouracil, *S*-ethyl-2-thiouracil) as well as purine derivative (theobromine) have been investigated.¹³⁸ The following reagents were employed: HgSO₄ + H₂SO₄, Hg(OAc)₂, MgO + CF₃COOH, Hg(OAc)₂ + HClO₄, and Hg(OCOCF₃)₂. It was found that only uracil is effectively mercured, affording 5-chloromercuiouracil in 85% yield after the treatment of the reaction mixture with KCl. In other cases, the mercuration of pyrimidine derivatives results in the formation of a mixture of the C(5)- and N-mercured compounds in low yields.¹³⁸ The mercury-containing heterocycles have been used¹³⁸ for the synthesis of the corresponding iodo-derivative by their treatment with a boiling aqueous KI₃ solution.

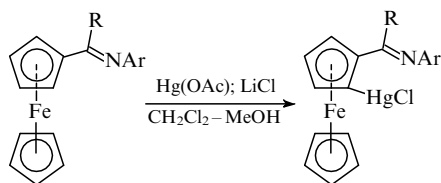
The effect of the mercurating system — a 1:1 mixture of mercury acetate with CF_3COOH — on ferrocene has been investigated.¹³⁹ It was established that, for the 1:1:1 ratios of the above reactants in an ether–alcohol mixture at room temperature, ferrocene is smoothly mercurated, giving rise to only the monomercurated product — ferrocenylmercury acetate (yield 86%). Under analogous conditions¹³⁹ but with the 2:2:1 reactant ratios, only the dimercurated product — 1,1'-diacetoxymercurioferrocene — is formed in 67% yield. These compounds are of considerable preparative interest for the synthesis of ferrocene derivatives.

The mercuration of arylferrocenes by treatment with $\text{Hg}(\text{OAc})_2$ in a CH_2Cl_2 – MeOH mixture and subsequent treatment of the reaction mixture with an aqueous solution of LiCl led to a mixture of three isomeric OMC, which were separated chromatographically.¹⁴⁰



$\text{R} = \text{Ph}, 4\text{-MeOC}_6\text{H}_4, 4\text{-ClC}_6\text{H}_4, 4\text{-NO}_2\text{C}_6\text{H}_4.$

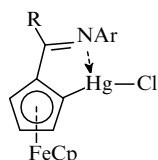
The mercuration of azomethines of the ferrocene series by mercury acetate has been described.^{141–146} After the addition of LiCl to the reaction mixture, the corresponding 2-chloromercurio-derivatives were isolated in 60%–85% yields in all cases.



$\text{R} = \text{H}, \text{Me}, \text{Ph}; \text{Ar} = 4\text{-MeOC}_6\text{H}_4, 4\text{-MeC}_6\text{H}_4, \text{Ph}, 4\text{-ClC}_6\text{H}_4, 4\text{-BrC}_6\text{H}_4, 4\text{-IC}_6\text{H}_4, 4\text{-NO}_2\text{C}_6\text{H}_4, 3\text{-ClC}_6\text{H}_4, 3\text{-BrC}_6\text{H}_4, 3\text{-NO}_2\text{C}_6\text{H}_4, \alpha\text{-C}_{10}\text{H}_7, \beta\text{-C}_{10}\text{H}_7, 2\text{-ClC}_6\text{H}_4.$

The structures of the substances synthesised were investigated by ^1H and ^{13}C NMR and X-ray diffraction methods.^{141, 144–146} In particular, the study of the ^{13}C NMR spectra for three series of 2-chloromercurioferrocenylimines ($\text{R} = \text{H}, \text{Me}, \text{Ph}$) led to the discovery of a satisfactory linear correlation between the chemical shifts of the carbon atoms in the ferrocenyl fragment and the Hammett constants σ_m and σ_p of the substituents in the arene ring.¹⁴⁵

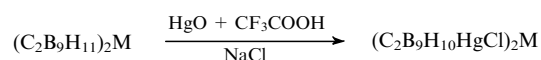
An intramolecular coordinate bond between the Hg and N atoms (2.087 Å) has been discovered in a series of 2-chloromercurioferrocenylimines on the basis of X-ray diffraction data for the latter. It proved to be shorter by 0.35–0.45 Å than the sum of the van der Waals radii of the nitrogen and mercury atoms.^{141, 144, 146}



$\text{R} = \text{H}, \text{Me}, \text{Ph}; \text{Ar} = \text{Ph}, 4\text{-ClC}_6\text{H}_4.$

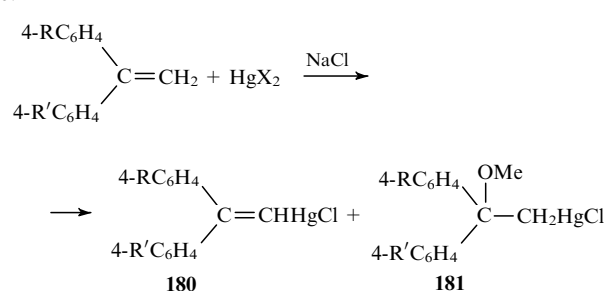
Pentakis(acetoxymercurio)pentamethylruthenocene has been obtained in 88% yield by the reaction of pentamethylruthenocene with mercury acetate (molar ratio 1:5) in the 1:1 ethanol–ether mixture.¹⁴⁷ It is halogenated on treatment with KI_3 or KBr_3 with formation of the corresponding pentahalopentamethylruthenocenes. The structures of the compounds have been established by X-ray diffraction.

The direct mercuration of *o*- and *m*-carbaboranes by treatment with HgO in CF_3COOH has been achieved.¹⁴⁸ It leads to the substitution of the hydrogen atom at the boron atom in the 9-position in the carbaborane ring by mercury. The mercuration of the dicarbaboranyl $\text{Fe}(\text{III})$,¹⁴⁹ $\text{Ni}(\text{IV})$, and $\text{Co}(\text{III})$ ¹⁵⁰ complexes takes place in the same position and under the same conditions.



$\text{M} = \text{Fe}, \text{Ni}, \text{Co}.$

1,1-Diarylethenes have an excess π -electron density, as a result of which it is possible to achieve their electrophilic vinylmercuriation on treatment with an equimolar amount of HgX_2 in acetonitrile or an ether–THF mixture with formation of compounds **180**.¹⁵¹



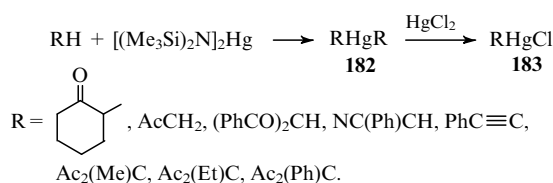
$\text{R} = \text{R}' = \text{H}, \text{Me}, \text{Cl}, \text{MeO}; \text{R} = \text{F}, \text{R}' = \text{MeO};$

$\text{R} = \text{Cl}, \text{R}' = \text{Me}; \text{X} = \text{BF}_4, \text{CF}_3\text{COO}.$

If the reaction is carried out in methanol, then electrophilic substitution and conjugate addition of the mercury salt to the double bond result in the formation of a mixture of the products **180** and **181**, the ratio of which depends on the initial reactant ratio.¹⁵¹

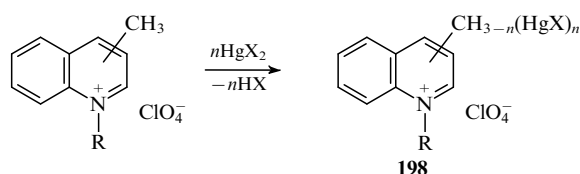
VII. Mercuration of CH acids

Apart from aromatic compounds, compounds with mobile hydrogen atoms, capable of giving rise to a stable carbanion, may be mercurated.¹⁵² The range of such compounds proved to be fairly wide.^{4–7} and it has been increasing continuously in connection with the synthesis of new substances and with the search for new mercurating agents. In particular, the reactions involving the α -mercuration of a large series of CH acids having $\text{pK}_a < 29$ with the aid of $\text{Hg}[\text{N}(\text{SiMe}_3)_2]_2$, have been investigated^{153, 154} which led to the synthesis of the symmetrical fully substituted OMC **182** in 50%–85% yield.³ Heating of compounds **182** with HgCl_2 in water or ethanol affords the corresponding chloromercurio-derivatives **183**.¹⁵³

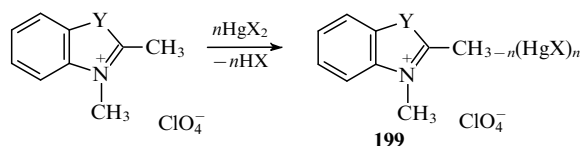


Weaker CH acids — acetonitrile and pinacoln ($\text{pK}_a > 31$) — could not be made to undergo this reaction.¹⁵³

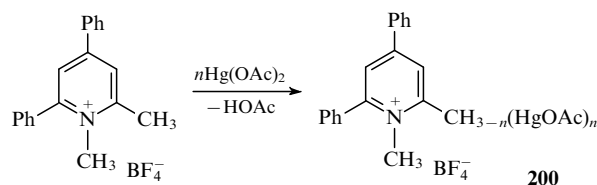
It has been observed recently⁹⁴ that MDNA readily mercurates compounds with mobile hydrogen atoms such as acetone, acetylacetone, and malonic, nitroacetic, and nitromalonic esters in nonpolar and polar organic solvents, as well as water. The mercuration of acetone and acetylacetone by MDNA at room temperature in ether leads to the substitution of only one hydrogen atom, whilst the mercuration of the nitroacetic and malonic esters under the same conditions affords dimercurated products.⁹⁴



R = Et, Ph; X = OAc, OCOCF₃; n = 1–3.

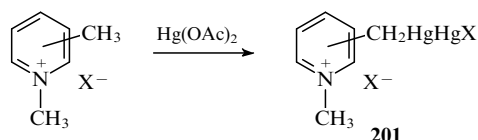


Y = O, S, NMe; X = OAc, OCOCF₃; n = 1–3.



n = 1–3.

However, the mercuration of 1,2- and 1,4-dimethylpyridinium salts under the same conditions yielded¹⁶⁴ the salts **201** with a Hg–Hg bond, which are stable at room temperature.



X = I, ClO₄, OAc.

We may note that in all the heterocyclic systems enumerated, only the methyl group in the α- or γ-position relative to the heteroatom is mercurated. The mercuration of the alkyl group (Me, Et) linked directly to the ring nitrogen atom has never been observed.

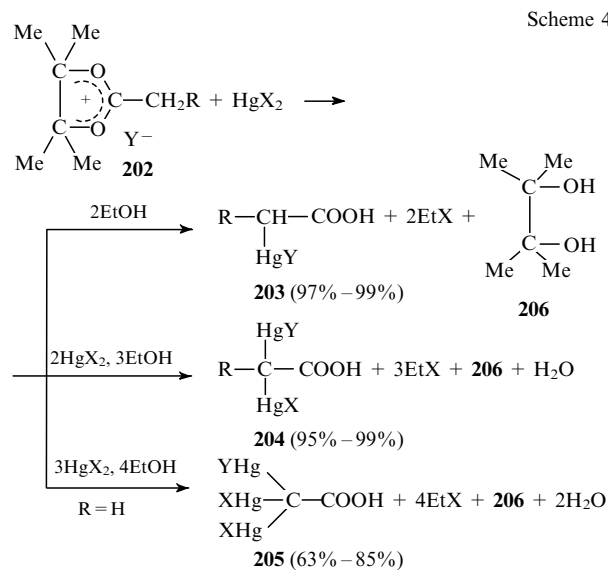
The structures of the salts **195**–**201** have been established^{160–164} by studying their chemical properties and on the basis of the results of elemental analysis, as well as ¹H NMR and IR spectroscopic data. The salts are of preparative interest for the synthesis of functionally substituted salts of heterocyclic cations, because the mercury-containing groups may be comparatively readily substituted by other groups.³

Furthermore, studies on the antimicrobial activities of the α-alkylmercurated pyrylium salts **195** and **196**, the pyridinium salts **200** and **201**, the quinolinium salts **198**, and the benzazolum salts **199** have shown¹⁶⁵ that this group of mercury-containing heterocyclic compounds possesses a striking antimicrobial activity with a wider activity spectrum than the familiar preparations.

Somewhat unusual results have been obtained¹⁶⁶ on mercuration of 2-alkyl-substituted 4,4,5,5-tetramethyl-1,3-dioxolanium salts **202** with mercury acetate or trifluoroacetate. In this case, the 1,3-dioxolane ring is opened in the course of mercuration on refluxing the reactants, which results in a high yield of α-mercurio-substituted carboxylic acids **203**–**205**, the ethyl esters of acetic or trifluoroacetic acid, and pinacol **206**. Depending on the molar reactant ratio, monomercurated (compound **203**), dimercurated (compound **204**), and trimercurated (compound **205**) carboxylic acids are obtained. According to elemental analysis and IR spectra,¹⁶⁶ the YHg group always enters into their compositions regardless of the nature of the mercurating agent (Scheme 4).

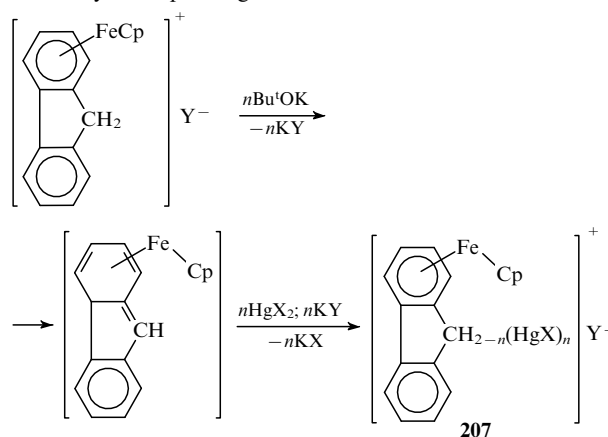
Thus the reactions constitute a convenient method of synthesis of α-mercurated carboxylic acids.

Successive treatment of the η⁶-fluorene-η⁵-cyclopentadienyl-iron cation with Bu⁺OK and HgX₂ mercury salts in a 1:1



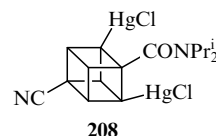
R = H, Me; Y = ClO₄, BF₄; X = OAc, OCOCF₃.

MeCN–dimethylcellosolve mixture led to the synthesis¹⁶⁷ of the corresponding mercury-containing complexes **207** for the first time. Mono- and di-mercurated compounds **207** are formed in 75%–82% yield depending on the molar reactant ratio.¹⁶⁷



X = OAc, OCOCF₃, Cl; Y = BF₄, PF₆; n = 1, 2; Cp = C₅H₅.

An interesting method for the mercuration of cubanes has been described for 4-cyano-1,1-diisopropylcarbamoylecubane as an example.¹⁶⁸ Successive treatment of the cubane with the lithium–tetramethylpiperidine–MgBr₂ system and then with HgCl₂ leads to the dimercurated cubane **208**.



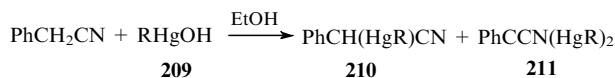
VIII. Mercuration by organomercury salts and hydroxides

The reactions presented in this section can be regarded as a direct method for the synthesis of asymmetric fully substituted OMC containing different types of Hg–element bonds.

The interaction of the organomercury hydroxides RgOH **209** (R = Ph, CH₂Ph, cyclo-C₆XH₁₁) with the nitriles PhCH(R')CN (R' = H, Et, Ph) has been investigated.¹⁶⁹

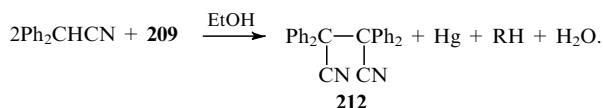
Depending on the nature of the group R in the molecule of the hydroxide **209** and the reaction conditions, mixtures of mono-mercurated (compound **210**) and dimercurated (compound **211**)

derivatives or only the dimercurated compounds are formed from phenylacetonitrile.¹⁶⁹ In the presence of small amounts (5%–10%) of KOH, only the dimercurated compounds **211** are obtained.

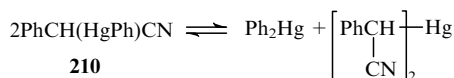


R = Ph, CH₂Ph.

Cyclohexylmercury hydroxide does not react with PhCH₂CN even in the presence of KOH. When Ph₂CHCN interacts with compound **209**, metallic mercury is liberated and the dimer **212** is formed, while PhCH(Et)CN does not react with compound **209** at all.¹⁶⁹

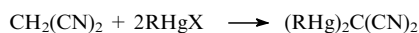


According to ¹⁹⁹Hg NMR data, compound **210** (R = Ph) is partly symmetrised in solutions in chloroform and pyridine.¹⁶⁹



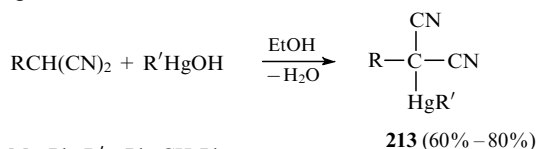
However, in the solid state it is an individual compound. This is indicated indirectly by the depression of the melting point (by 20–25 °C) of the prepared mixture of compound **210** and HgPh₂. IR and NMR spectroscopic data have shown that compounds **210** and **211** exist mainly as the C-form.¹⁶⁹

Treatment of malonodinitrile with RHgX leads to the formation of only the dimercurated product.¹⁷⁰



R = Ph, CH₂Ph; X = OH, OAc.

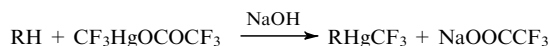
The organomercury derivatives **213**, which exists mainly in the C-form, have been obtained by treating the substituted dinitriles RCH(CN)₂ with organomercury hydroxides R'HgOH or acetates R'HgOAc.¹⁷¹



R = Me, Ph; R' = Ph, CH₂Ph.

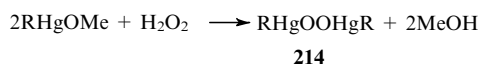
It is of interest to note that a degenerate exchange reaction, occurring with dissociation of the C–Hg bond, has been observed¹⁷¹ for the phenylmercury derivative of methylmalonodinitrile.¹⁷¹ Nevertheless, the organomercury dinitriles **213** are not symmetrised in solution,¹⁷¹ in contrast to the organomercury derivative of phenylacetonitrile **210** investigated earlier.¹⁶⁹

The organomercury salt CF₃HgOCOCF₃ interacts readily⁸⁸ with unsaturated compounds capable of being deprotonated in an alkaline medium.



R = PhC≡C, Cl₂C=CCl.

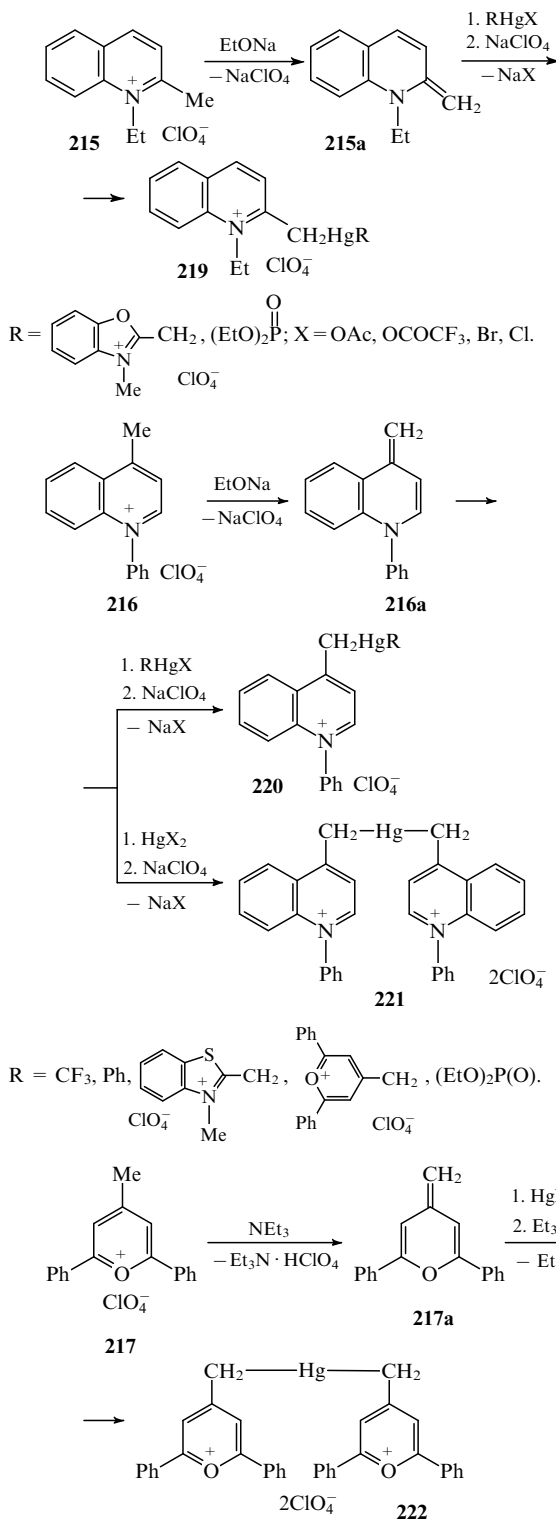
The reaction of RHgOMe with hydrogen peroxide in methanol afforded the OMC **214**.¹⁷²

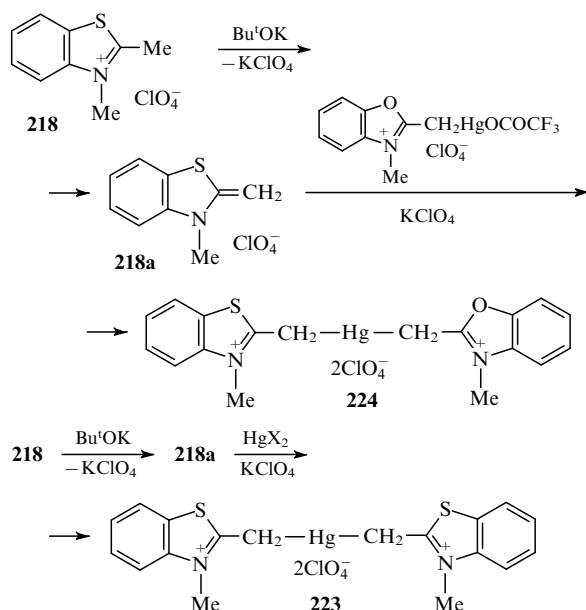


In benzene, diethyl ether, and methylene chloride, compounds **214** interact with an excess of H₂O₂ and are converted into the

hydroperoxides RHgOOH. However, according to IR spectroscopic data,¹⁷² the latter are complexes of the type (RHgO)₂·H₂O₂

A new method of synthesis of fully substituted mercury-containing salts of heterocyclic cations has been described.¹⁷³ Successive treatment of 2- and 4-methylquinolinium (compounds **215** and **216**), 4-methyl-2,6-diphenylpyrylium (compound **217**), and 1,2-dimethylbenzothiazolium (compound **218**) perchlorates with an equimolar amount of a base (EtONa, Bu^tOK, NEt₃) and then with an equimolar amount of organomercury salts RHgX led to the synthesis¹⁷³ of the fully substituted 4-methylenemercury-containing salts of the corresponding heterocyclic cations **219–224** in 61%–83% yield.

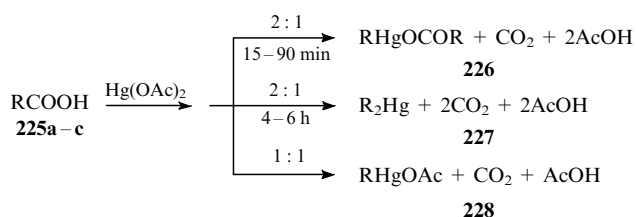




Thus the reactions involving the mercuriation of the methylene derivatives of the heterocyclic bases **215a**–**218a** by mercury salts or organomercury reagents presented above make it possible to obtain diverse symmetrical (compounds **221**–**223**) and asymmetric (compounds **219**, **220**, and **224**) fully substituted 2- and 4-methylenemercuro salts of heterocyclic cations. The method is simple to use and is extremely general, and is therefore promising for the synthesis of new OMC.

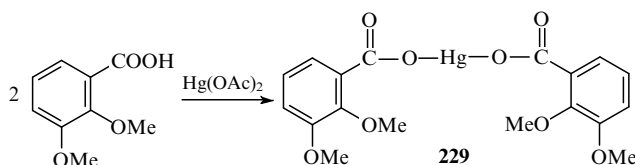
IX. Other methods of synthesis of organomercury compounds

The interaction of polymethoxybenzoic acids **225** with mercury acetate in proportions of 2:1 proceeds in an unusual manner, leading even under mild conditions (aqueous methanol, 20 °C, 15–90 min) to different decarboxylation products **226**–**228** depending on the molar reactant ratio and the reaction time.¹⁷⁴

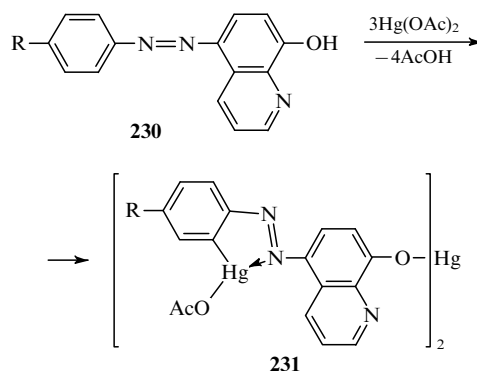


$\text{R} = 2,6\text{-(MeO)}_2\text{C}_6\text{H}_3$ (**a**); $2,3,4\text{-(MeO)}_3\text{C}_6\text{H}_2$ (**b**); $2,4,6\text{-(MeO)}_3\text{C}_6\text{H}_3$ (**c**).

The reaction of $\text{Hg}(\text{OAc})_2$ with 2,3-dimethoxybenzoic acid leads to the mercury salt **229**, while in the case of 3,4,5-trimethoxybenzoic acid the reaction does not proceed at all.¹⁷⁴



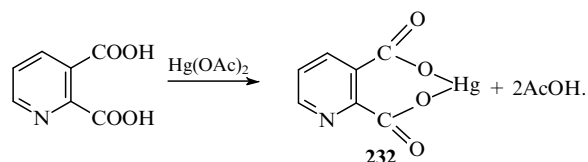
The azo-coupling reaction of compound **230** with $\text{Hg}(\text{OAc})_2$ proceeds with formation of the products of dimercuriation at the carbon and oxygen atoms (compound **231**).¹⁷⁵



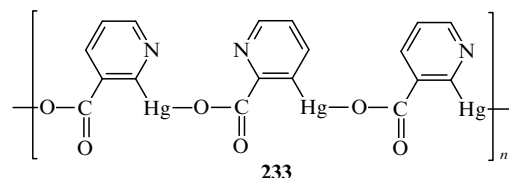
$\text{R} = \text{H}, \text{Me}, \text{NO}_2$.

On the other hand, treatment of compound **230** with HgCl_2 results in the formation of only a 1:1 complex, the structure of which has not been established.¹⁷⁵

The interaction of quinolinic acid with mercury acetate in aqueous acetic acid leads to the formation of mercury pyridine-2,3-dicarboxylate **232**.¹⁷⁶



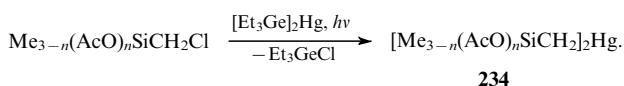
A 9:1 mixture of 2-carboxylatopyridin-3-ylmercury and 3-carboxylatopyridin-2-ylmercury, which according to the authors have a polymeric structure of type **233** with a C–Hg–O linkage, has been obtained by the decarboxylation of the **232** in DMSO at 190 °C for 1 h.



$n = 2-3$.

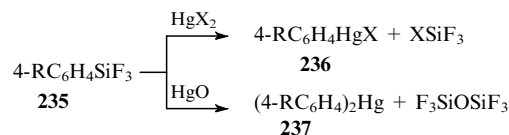
The structures of compounds **232** and **233** have been confirmed by IR and ^1H , ^{13}C , and ^{199}Hg NMR spectroscopic data as well as mass-spectrometric data.¹⁷⁶

A method has been developed¹⁷⁷ for the synthesis of bis(acetoxysilylmethyl)mercury compounds **234** in 80%–90% yields. It is based on the photoinitiation reaction of bis(triethylgermyl)mercury with acetoxychloromethylsilanes.



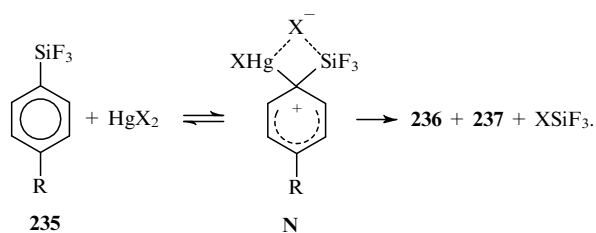
The structure of the mercury compounds **234** has been confirmed by NMR spectroscopic data. It has been noted that $^2J(\text{Hg}-\text{Si})$, $^2J(\text{Hg}-\text{H})$, and $^2J(\text{Hg}-\text{C})$ increase with increase in the number of acetoxyl-groups bound to the silicon atom.¹⁷⁷

When the Si–C bond in aryltrifluorosilanes **235** dissociated on treatment with mercury salts HgX_2 or HgO , asymmetric (compound **236**) and symmetrical (compound **237**) OMC are formed in high yields.¹⁷⁸



$\text{R} = \text{H}, \text{Me}, \text{Cl}, \text{Br}, \text{NO}_2$; $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{CN}, \text{OAc}$.

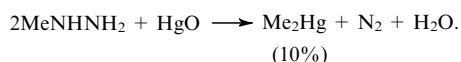
It has been noted that electron-donating substituents facilitate the above reactions, whilst electron-accepting ones hinder them. This permits certain conclusions about the reaction mechanism, which can be represented by the following scheme in a general form:⁸



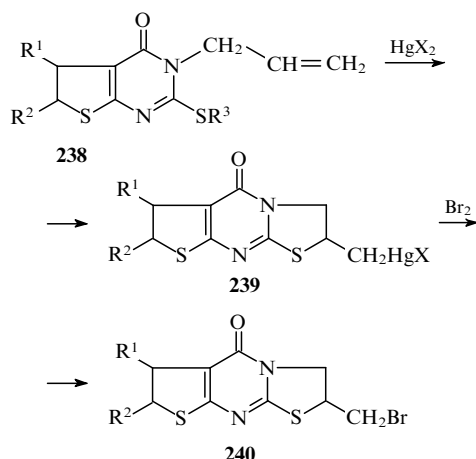
There is no doubt that the more effective stabilisation of the cyclic transition state N as a result of the delocalisation of the positive charge is attained in the case of electron-donating substituents R, which thus promote the formation of the corresponding reaction products **236** and **237**.

Mercury salts HgX and HgO also cleave the Si–C bond in chloromethyltrifluorosilanes F₃SiCH_{3–n}Cl_n (*n* = 1–3) with formation of the corresponding derivatives XHgCH_{3–n}Cl_n or Hg(CH_{3–n}Cl_n)₂ in 18%–30% yields.¹⁷⁸ The replacement of a fluorine atom in organyltrifluorosilanes by an alkyl group hinders the cleavage of the Si–C bond.

A method of synthesis of dimethylmercury by the interaction of methylhydrazine with mercury oxide in diethylether has been described.¹⁷⁹



The interaction of mercury salts with derivatives of thieno[2,3-*d*]pyrimidines **238** has been achieved.¹⁸⁰ It was shown that the solvatomercuration of compound **238** in ethanol or methanol is accompanied by their intramolecular cyclisation with participation of the sulfur atom of the thioureide group, which leads to the formation of the tricyclic system **239** with a mercury-containing substituent.



R¹ = R² = Me; R¹ + R² = (CH₂)₃, (CH₂)₄; R³ = H, COPh; X = Cl, Br.

The structure of the tricyclic system **239** has been confirmed by ¹H NMR and IR spectroscopic data and also by the reaction with bromine, which leads to the bromo-derivatives **240** already known.¹⁸⁰

X. Conclusion

The data examined in the present review show that studies designed to expand the applications of already known methods and to develop new methods of synthesis of organomercury compounds have been prosecuted vigorously in recent years.

This has led to the availability of a wide range of organomercury compounds in which mercury is bound to fragments of diverse organic molecules — aliphatic, carbocyclic, aromatic, heterocyclic, organometallic, *etc.* The range of the possible practical ways of using the mercury-containing compounds obtained is extremely wide.^{2,7} Thus many of the newly synthesised compounds can be regarded as potential medicinal preparations with antibacterial^{113,115} and antimicrobial^{126,134,165} properties and also as chemical agents for the protection of plants, acting as nematocides,^{128,129,137} fungicides,^{128,129} and insectoacaricides.¹²¹

Thus the search for and development of new methods of synthesis of organomercury compounds have not lost current interest because these compounds have found applications in various branches of science, industry, medicine, and agriculture.

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Natural polysulfides

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Contents

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Abstract. The structures of natural polysulfides of animal and plant origin are considered. Data are presented on the biological activity of compounds containing di-, tri-, tetra-, and pentasulfide groups. Schemes of total synthesis of the above-mentioned compounds and their structural analogues are discussed. The bibliography includes 156 references.

I. Introduction

Natural organosulfur compounds are abundant and structurally very diverse. The present review is dedicated to a group of natural organosulfur compounds that is scantily reviewed, viz., to di-, tri-, and polysulfides of plant, animal, and microbial origin. The questions pertinent to the chemistry of peptides containing a disulfide fragment are omitted from the discussion, since they have been adequately addressed in the literature (see, for example, Ref. 1).

The chemistry of simple dialkyl polysulfides of plant origin has been discussed in a number of reviews;^{2–4} therefore we shall restrict our consideration to a mere mention of the discovery of a particular substance in natural objects and discuss only those questions that are related to their biological activity.

The main subjects to be considered in the review are structurally more complex low- molecular-weight di-, tri-, tetra-, and pentasulfides. They constitute a not very abundant group of natural compounds; however, in our opinion, their structures and properties are so remarkable that they deserve special discussion.

One of the major goals of this review is to attract the attention of investigators working in the field of biologically active compounds to problems of modelling of natural sulfur-containing structures and elaboration of schemes of total synthesis of the most promising representatives of this class.

II. Natural di- and poly-sulfides, their conversions, and biological activity

1. Aliphatic di- and poly-sulfides

Aliphatic disulfides with a simple structure are the constituents of essential oils of certain plants responsible for their unpleasant odour.^{5,6} For example, the essential oil obtained by steam distillation of *Ferula illiensis* Krash. roots contains 62% of *E*- and *Z*-isomeric *sec*-butyl propenyl disulfides and a small amount of *sec*-butyl methyl- and di-*sec*-butyl disulfides.^{7,8} The *sec*-butyl propenyl disulfide has been also isolated from the essential oil of *Ferula asa foetida*.⁶ The gum of this umbellate plant contains also methylthio derivatives of allyl sulfides: Bu^sSSCH=CHCH₂SMe and PrⁿSCH₂CH=CHSSMe.

The Indian tree *Azadirachta indica* known for its potent insecticidal action produces, along with unique antifeedants of the terpenoid series (azadirachtins), also volatile polysulfides. Thus the isolation of diisopropyl di-, tri-, and tetra-sulfides as well as allylpropyl di-, tri-, and tetra-sulfides has been described.⁹ It is reported that dipropyl disulfide possesses a strong larvicidal action and suppresses the reproduction of the tiger mosquito *Aedes aegypti* and the tobacco worm *Heliothis virescens*.

The curative properties of garlic and onion have been known from time immemorial. Contemporary medicine considers the therapy with preparations of garlic or onion as a prospective trend in the treatment of atherosclerosis, coronary thrombosis, asthma, and microbial infections.^{10–12} Studies into the structure of the active principles of garlic and onion were undertaken in the last century. Thus steam distillation of garlic gives diallyl di-, tri-, and tetra-sulfides.¹³ These compounds are formed in the course of thermal or hydrolytic treatment of native substances. The latter include alliin, [(+)-*S*-allyl-L-cysteine *S*-oxide] (**1**) first isolated from the alcoholic extract of the garlic *Allium sativum* and possessing a strong bactericidal action.¹⁴ Intact garlic cloves contain up to 0.24% of alliin **1**, which is converted into *S*-allyl prop-2-ene thiosulfinate (allicin, **2**) by allinase.¹⁵ This conversion passes through the stage of formation of prop-2-ene sulfenic acid, which is further self-condensed into alliin. Allicin **2** is the main component responsible for the specific odour of garlic.

Alliin **1** constitutes 83% of the total amino acid content of garlic, 13% goes to *S*-methylcysteine *S*-oxide (**3**), and 2% to the amino acid (**4**).¹⁶ Enzymic cleavage of the amino acid **3** with allinase results in *S*-methyl methanethiosulfinate (**5**). *S*-Allyl-cysteine *S*-oxide **1** undergoes similar cleavage to give *S*-allyl methanethiosulfinate (**6**).¹⁷

The high reactivity of allicin **2** and the occurrence of other types of biochemical cleavage of alliin result in the formation of a large number of di- and tri-sulfides and their monosulfoxides

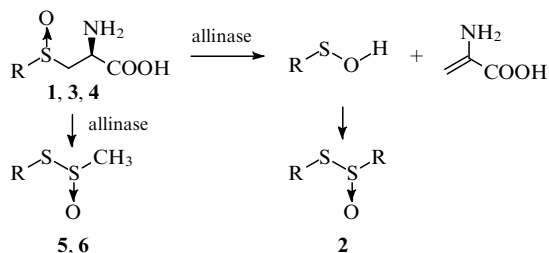
G A Tolstikov, E E Shul'ts Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences, prosp. akad. Lavrent'eva 9, 630090 Novosibirsk, Russian Federation. Fax (7-383) 235 47 52. Tel. (7-383) 235 16 46 (G A Tolstikov), Tel. (7-383) 235 16 55 (E E Shul'ts).

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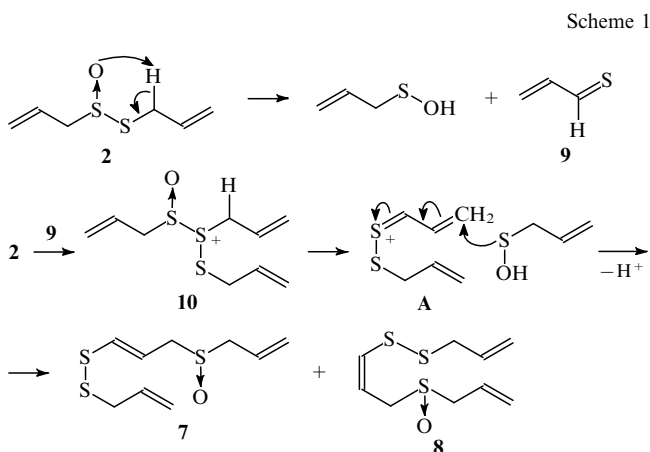
carrying different substituents. Thus a rather complex mixture of disulfides and thiosulfonates has been obtained by allinase treatment of a mixture of amino acids **1**, **3**, and **4**.



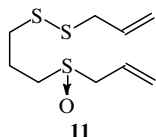
R = CH₂CH=CH₂ (**1**, **2**, **6**); Me (**3**, **5**); Prⁿ (**4**).

Many products of steam distillation of various garlic species are identical. Thus, it has been reported that the essential oil of the South American garlic *Adenocalumma alliaceum* contains 62% of diallyl di- and diallyl tri-sulfides.¹⁸

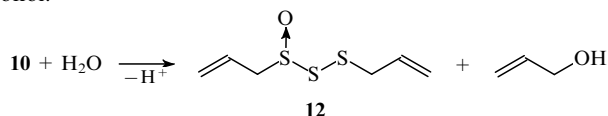
It has been established that the antithrombotic activity of garlic extracts increases upon their heating and concentration (IC₅₀ = 0.3–50 μg ml⁻¹). Their ability to prevent coronary thrombosis and atherosclerosis and increase blood coagulation time is currently ascribed to the presence of *E*- (**7**) and *Z*-achoenes (**8**), 4,5,9-trithiadodeca-1,6,11-triene-9-oxides.¹⁹ It is assumed that achoenes are formed from alliin according to Scheme 1.



β-Elimination in alliin gives thioacrolein (**9**) and prop-2-enesulfenic acid. *S*-Allylthiolation of alliin results in the sulfonium ion **10**, which undergoes β-elimination to the sulfonium ion **A**. Subsequent γ-addition of prop-2-enesulfenic acid to the cation **A** gives achoenes **7** and **8**. Boiling of alliin in aqueous methanol gives 17% of a 4:1 mixture of achoenes **7** and **8**. One of the products of alliin conversion is dihydroachoenes (**11**).²⁰

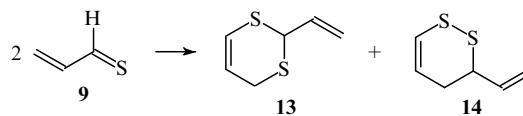


Another pathway of intermediate **10** conversion consists in the addition of a water molecule at the allylic double bond eventually resulting in 4,5,6-trithianona-1,8-diene-4-oxide (**12**) and allyl alcohol.

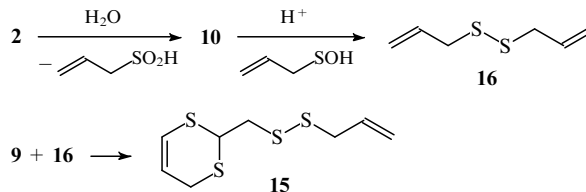


The involvement of intermediate thioacrolein **9** in the [4+2]-cyclic addition accounts for the formation of minor components of the extracts: 2-vinyl-4*H*-1,3-dithiine (**13**), 3-vinyl-3,4-dihydro-1,2-dithiine (**14**), and 2-(2,3-dithia-hex-5-enyl)-4*H*-1,3-dithiine

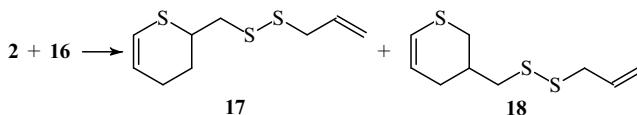
(**15**). It is noteworthy that these dithiacyclanes have been identified among other compounds isolated from extracts and distillates of garlic.²¹



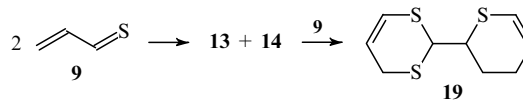
The results of studies concerned with chemical conversions of garlic components have been discussed.^{22,23} Vacuum pyrolysis of diallyl disulfide (**16**) formed from alliin **2** upon the interaction of the intermediate **10** with water gives dithiines **13** and **14** in a 4.4:1 ratio. Dimerisation of thioacrolein **9** in the presence of disulfide **16** results in a tetrasulfide **15**.



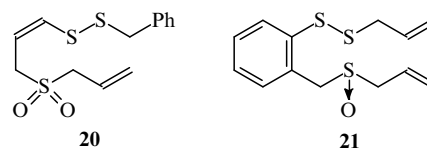
The thermal reaction between alliin **2** and disulfide **16** is accompanied by the formation of thio analogues of dihydropyranyl derivatives of disulfides, compounds **17** and **18**. The mechanism of this reaction is still unclear.²⁴



Of special interest are thioacrolein reactions. In addition to the aforementioned cyclodimerisation resulting in disulfides **13** and **14** (the dimerisation at 170 K gives a mixture of these dithiines in a 9:1 ratio in a 25% yield), the formation of the thioacrolein trimer, [2-(3,4-dihydrothiopyran-2-yl)-4*H*-1,3-dithiine (**19**)] takes place.²⁵

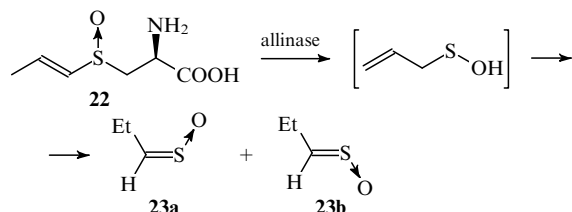


The high antithrombotic activity of achoenes **7** and **8** and dithiines **13** and **14** has stimulated the studies aimed at the synthesis of their analogues. It has been shown, in particular, that disulfides **20** and **21** possess twice as large an antithrombotic activity as *Z*-achoenes (**8**).²⁰ This finding opens up interesting perspectives in the elaboration of valuable therapeutic drugs.

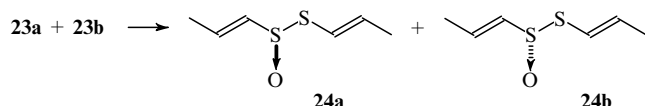


Organosulfur compounds of onion of the *Allium* genus are no less interesting. Early studies report the identification of ethyl propyl and ethyl isopropyl disulfides, butyl propyl and butyl isopropyl disulfides, diallyl disulfide, diallyl trisulfide, methyl propyl and allyl methyl tetrasulfides, allyl propyl tetrasulfide, dimethyl pentasulfide, and methyl propyl pentasulfide as the components of the onion *Allium cepa*.^{26,27} Wild varieties of onions of the *Allium* genus contain dipropyl disulfide and allyl methyl trisulfide.^{28,29} The essential oil of the onion *Allium cepa* contains no less than 100 compounds of which 39 organosulfur compounds have been reliably identified.³⁰ Methyl propyl disulfide, dipropyl disulfide, (*Z*)- and (*E*)-allyl propyl disulfide, dipropyl trisulfide, (*Z*)- and (*E*)-allyl methyl trisulfides, (*Z*)- and (*E*)-allyl propyl trisulfides, methyl propyl tetrasulfide, dipropyl tetrasulfide, (*Z*)-

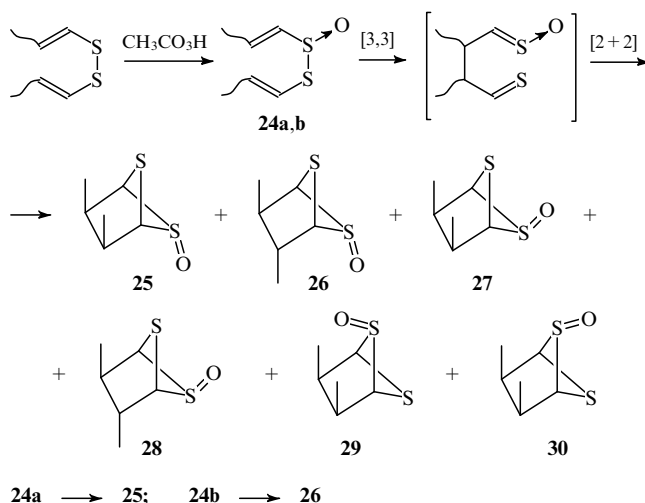
and (*E*)-allyl propyl tetrasulfides, dimethyl pentasulfide, and methyl propyl pentasulfide are the major components. The ratio of allyl, methyl, and *n*-propyl residues is 85 : 13 : 2; diallyl disulfide makes up 30%–50% of the total mixture.²⁹ In addition to the polysulfides mentioned above, steam-distillation products have been found to contain cyclic and acyclic vinyl thiosulfonates. [(+)-*S*-(*E*-Propenyl)-L-cysteine *S*-oxide] (**22**), the amino acid isomeric to alliin, is the precursor of organosulfur components. Its enzymic cleavage gives stereoisomeric propanethioaldehyde *S*-oxides (**23a,b**), of which the former predominates.



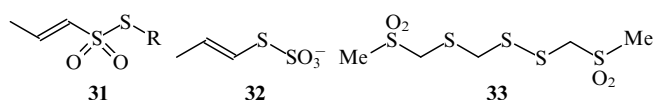
Both compounds are responsible for lacrymatory properties of the onion. Their self-condensation results in the formation of *S*-*E*-propenyl *E*-prop-1-enethiosulfonates (**24a,b**). The condensation involves the intermediate prop-1-enesulfenic acid and methane- and propanesulfenic acids formed upon enzymic cleavage. Compounds **23a,b** and **24a,b** are the main carriers of the onion odour.³⁰



Zwiebelans — 1 α ,2 α ,3 α ,4 α ,5 β - and 1 α ,2 α ,3 β ,4 α ,5 β -2,3-dimethyl-5,6-dithiabicyclo[2.1.1]hexane-5-oxides (**25**, **26**) — are also the onion flavourants. Their formation is accounted for by a transformation of dipropenyl disulfide monosulfoxide, which involves the Cope rearrangement as the first step followed by [2 + 2]-cycloaddition. When a mixture of stereoisomeric dipropenyl disulfides had been used, the reaction gave six dithiabicyclanes (**25**–**30**).³¹ The synthesis of dithiabicyclanes in plants is stereospecific: *S*-(*E*)-prop-1-enyl (*E*)-prop-1-enylthiosulfonate (**24a**) gives zweibelan **25**, whereas the *Z*-isomer **24b** gives zweibelan **26**.³²

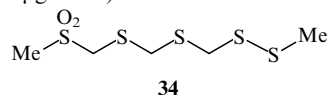


The high biological activity of dithiabicyclo[2.1.1]hexane derivatives can be inferred from the fact that a mixture of zweibelans **25** and **26** isolated from *Allium cepa* extracts inhibits by 65%–90% the biosynthesis of leukotriene TXB₂ in human cells when used in concentrations of 0.1–1.0 mg ml^{−1} (see Ref. 31). The identification of thiosulfonates **31** and Bunte salts **32** in onion extracts has been reported.³¹

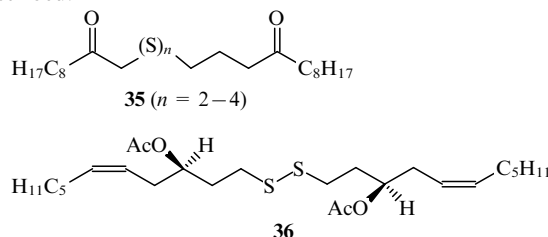


The medicinal plant *Dysoxylum richii* growing in the Fiji Islands is used by the local population as a tea additive and a means of prophylaxis against diseases caused by pathogenic microorganisms. The active principle of this plant is dysoxysulfone, 2,4,5,7,9-pentathiadecane-2,2,9,9-tetraoxide **33**, which is a potent inhibitor of the proliferation of *Staphylococcus aureus*, *Bacillus subtilis*, and *Candida albicans*. The minimum inhibiting concentrations (MIC) of **33** for these microorganisms are 100, 20 and 10 μ g plate^{−1}, respectively.³³ In addition, this compound manifests high antitumour activity against human ovarian carcinoma cells (IC₅₀ = 5 μ g ml^{−1}; the corresponding value for large intestinal adenocarcinoma is 7.4 μ g ml^{−1}).³² This plant is the second representative of the *Meliaceae* family after *Azadirachta indica* that produces sulfur-containing metabolites.

High antitumour activity has also been observed for 2,3,5,7,9-pentathiadecane-9,9-dioxide **34** isolated from the 'Shitake' fungus *Lentinus edodes* (IC₅₀ for murine leukemia cells is 0.62 μ g ml^{−1}).³⁴

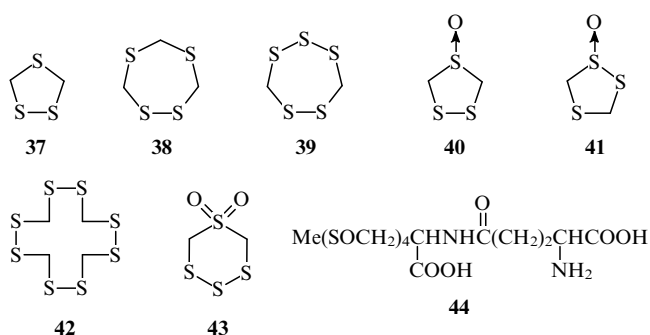


The Hawaiian sea algae *Dictyopteris plagiogramma* are rich in saturated and unsaturated linear C₁₁ hydrocarbons. The isolation of oxo-oligosulfides **35** and diacetoxysulfide **36**, which can be considered as precursors of undeca-1,3,5-trienes, has been described.^{35–37}



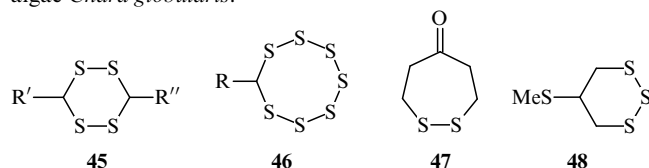
2. Saturated cyclic di- and poly-sulfides

Cyclic oligo- and poly-sulfides **37**–**43** have been isolated and identified as carriers of antibacterial activity in extracts of the red algae *Chondria californica*.³⁸ These thiacyclanes can be regarded as the products of condensation of formaldehyde with hydrogen sulfide. The highest antibiotic activity in this series of compounds is manifested by 1,2,3,5-tetrathiane-5,5-dioxide (**43**), which inhibits the growth of *Vibrio anguillarum*, *Proteus mirabilis*, *Salmonella typhimurium*, and *E.coli* in a concentration of 10 μ g ml^{−1}. Sulf-oxides **40** and **41**, which can be obtained from 1,2,4-trithiolane **37**, also possess antibiotic activity. 1,2,3,5,6-Pentathiepane (**39**) is identical to the so-called lenthionine produced by the fungus *Lentinus edodes*. Lenthionine is biogenetically related to lenthinic acid (**44**).³⁹ Extracts of other *Chondria* species are devoid of antimicrobial activity and do not contain cyclic polysulfides.



Cyclic polysulfides of the type 1,2,4-trithiolane (**37**), 1,2,3,5,6-pentathiepane (**39**), 1,2,4,5-tetrathiane (**45**), and 1,2,3,4,5,6,7-heptathiocane (**46**) have been isolated from the cultural fluid produced by *Thermococcus* cells.⁴⁰ Studies of biological activity of these compounds have revealed that the highest fungicidal activity is exerted by pentathiepane **39** ($7.8 \mu\text{g ml}^{-1}$ with respect to *Microsporum canis*). The *in vitro* antihelminthic activity against *Caenorhabditis elegans* has been established for thiolane **37**. It has been found that alkyl-substituted polysulfides **46** are unstable and decompose to yield sulfur and disubstituted cyclic polysulfides.

Saturated six- and seven-membered di- and tri-sulfides are rather rare. So far only one seven-membered cyclic disulfide **47** isolated from the alga *Dictyopteris plagiogramma* is known.³⁵ 5-Methylthio-1,2,3-trithiane (**48**) has been isolated from the green algae *Chara globularis*.⁴¹



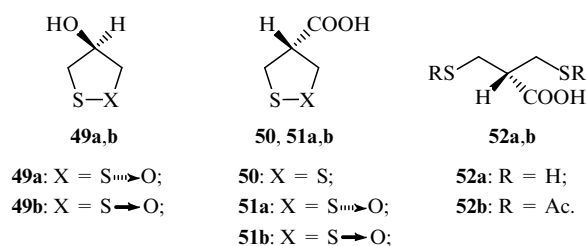
3. 1,2-Dithiolanes and their derivatives

Of great biological importance are functionally substituted derivatives of 1,2-dithiolane isolated from animal and plant objects.

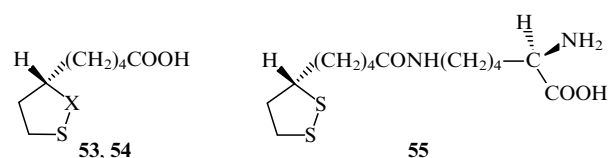
Thus the diastereoisomeric 1,2-dithiolane-1-oxides brugierol (**49a**) and isobrugierol (**49b**), which control plant growth have been isolated from the methanolic extract of the bark of *Brugiera conjugata*.^{42, 43}

A potent plant growth inhibitor, whose action is similar to that of abscisic acid, is asparagusic (1,2-dithiolane-4-carboxylic) acid (**50**) isolated from young sprouts of asparagus (*Asparagus officinalis* L.).⁴⁴

Asparagusic acid sulfoxides (**51a,b**) obtained by extraction of asparagus sprouts with methanol manifest high growth-regulating activity.⁴⁵ It is noteworthy that dihydroasparagusic acid (**52a**) and its diacetate (**52b**) have also been isolated from the asparagus plant. This suggests that asparagusic acid plays the key role in the biochemically important process of acetyl group transport mediated by acetyl-CoA.

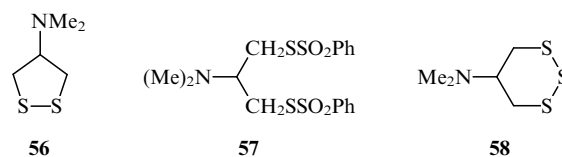


This group of disulfides includes lipoic acid (**53**) and its sulfoxide, β -lipoic acid (**54**), present in both animal and plant organisms. Lipoic acid plays the role of an acetyl group transfer factor and a factor promoting the growth of bacteria and *Protozoa*. In the form of protein-bound ϵ -lipoyllysine (**55**), lipoic acid and its reduced form, dihydrolipoic acid, are the coenzymes for pyruvate dehydrogenase and α -ketoglutarate dehydrogenase responsible for oxidative decarboxylation of α -keto acids with the transfer of the acetyl group to coenzyme A. The participation of lipoic acid in thiol-disulfide conversions of proteins, oxidative phosphorylation, and arachidonic acid conversion into prostaglandin H has also been established.^{1, 46} Lipoic acid participates in the primary step of the quantum of light conversion in photosynthesis.⁴⁷ In the form of vitamin N, lipoic acid is used in the treatment of liver disorders, diabetes, atherosclerosis and other diseases resulting from disturbances in lipid metabolism.

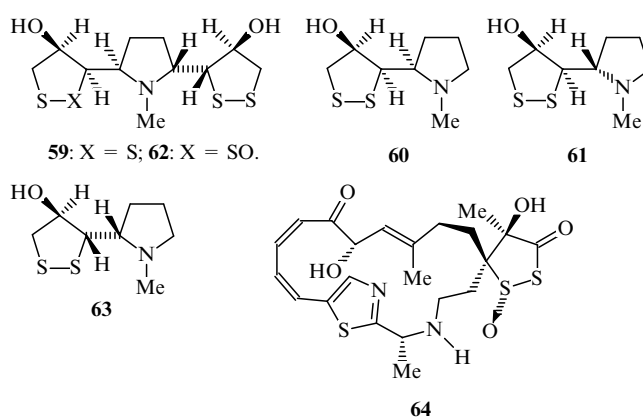


X = S (**53**), SO (**54**).

4-Dimethylamino-1,2-dithiolane — nereistoxin (**56**) — isolated from the sea worm *Lumbriconereis heteropoda* possesses unique insecticidal activity.^{48, 49} This simple molecule has served as a model in the synthesis of highly effective insecticides.⁵⁰ For example, the compound bensultap (**57**), which exhibits high selectivity against Coleoptera,⁵¹ has been recommended for suppressing the reproduction of the Colorado potato beetle without any detriment to beneficial insects, bees, and fish. The practical application of 5-dimethylamino-1,2,3-trithiane (**58**) as insecticide has been reported.^{49, 52}



The bark of the Brazilian tree *Cassipourea guianensis* contains a group of alkaloids of the 1,2-dithiole type. The main component of the extract, gerardin (**59**), is a potent fungistatic agent. Quinesins A, B, C, and G (compounds **60–63**, respectively) possess high insecticidal activity.^{53–55} The antibiotic leunamycin (**64**) produced by *Streptomyces* sp. and possessing strong anti-tumor activity^{56, 57} is also a 1,2-dithiole derivative.

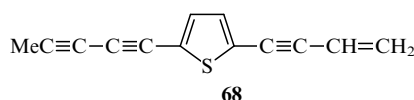
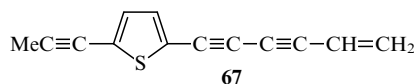
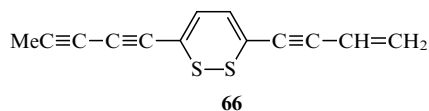
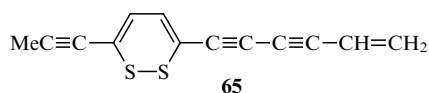


4. 1,2-Dithiins

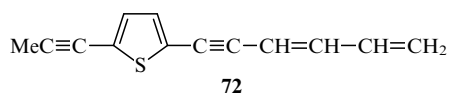
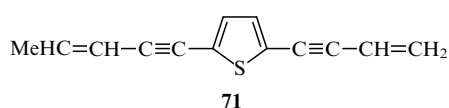
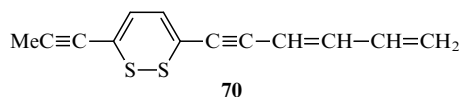
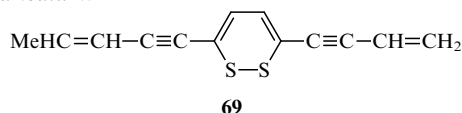
Increasing attention is presently focussed on a novel class of sulfur-containing heterocyclic compounds, 1,2-dithia-cyclohexa-3,5-dienes, in connection with their unusual structure and a broad spectrum of biological activity. Thus very promising candidates for antiviral and antibacterial agents are acetylenic derivatives of this heterocycle. Red coloured thiarubins A (**65**) and B (**66**) are produced by many plants used as curative agents in the folk medicine of some African countries. For example, leaves of the African plant *Aspilia africana*, which contain thiarubins A and B, are used for the treatment of abdominal infections. It has been noted also that these leaves are chewed by chimpanzees.⁵⁸ 3-(Hex-5-en-1,3-diynyl)-6-(1-propynyl)-1,2-dithiin **65** possesses antiviral, fungicidal, and antibacterial activities (when used at a concentration of $10^{-7} \text{ mg ml}^{-1}$) and inhibits the growth of *Candida albicans* at the level of the drug funizone.⁵⁹

Other sources of thiarubins are: *Aspilia mossambicensis*, *A. plurisetta*,⁶⁰ *Ambrosia artemisiifolia*,⁶¹ *Pegolettia senegalensis*,⁶² *Wedelia hookeriana*,⁶³ *Schkhuria multiflora*,⁶⁴ *S. senecioides*,⁶⁵ *Chaenactis douglasii*, *Eriophyllum lanatum*⁶⁶ and *Eriophyllum caespitosum*.^{65, 67}

It is noteworthy that thiarrubins are present in the plants together with the corresponding thiophenes (**67**, **68**).⁶⁸



Some plants of the *Compositae* family produce dihydrothiarrubins (**69**, **70**) and thiophenes genetically linked to them (**71**, **72**). For instance, dithiin **69** has been isolated from *Picradeniopsis woodhousei*,⁶⁹ *Lasthenia*,⁷⁰ and *Ogedaea boliviana*,⁷¹ whereas 2,5-disubstituted thiophene **72** is present in the plant *Melampodium divaricatum*.⁷²



3-Vinyl-3,4-dihydro-1,2-dithiin (**14**) isolated from garlic has been also identified among compounds that determine the odour of cooked asparagus.⁷³

The chemistry of 1,2-dithiin derivatives has been reviewed.⁷⁴

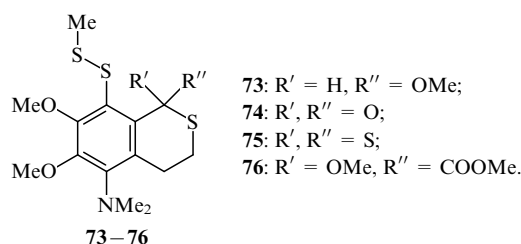
5. Di- and poly-sulfides carrying aromatic or heteroaromatic substituents

Di- and poly-sulfides having in their structure a functionalised aromatic or heterocyclic (imidazoline, thiazole) fragment possess valuable biological activity. Compounds, in which these fragments are either linked together with S–S bonds, or contain a cyclic polysulfide fragment or a terminal methylthio substituent, have been isolated.

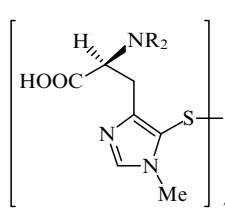
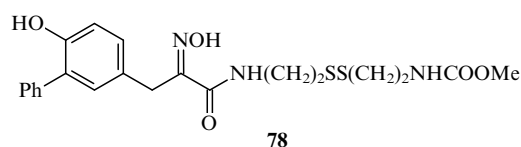
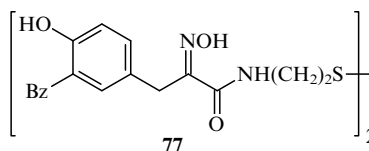
Thus polycarpamines A–D (compounds **73**–**76**) isolated from the ascidia *Polycarpa aurata* manifest high *in vitro* inhibitory activity against *Candida albicans* and *Saccharomyces cerevisiae*.⁷⁵ The sponges *Psammoplysilla purpurea* contain psammoplysins A (**77**) and D (**78**) suppressing the growth of the gram-positive bacteria *Staphylococcus aureus* and *Trychophyton mentagrophytes*.⁷⁶

Amino acids of unusual structure **79** have been isolated from the starfish *Astropecten latespinatus*. They exhibit cytotoxic activity against KB-cells ($IC_{50} = 3 \times 10^{-6}$ mg ml⁻¹).⁷⁷

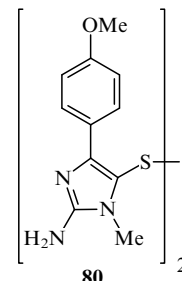
The disulfide polycarpine (**80**) has been recently isolated from a methanolic extract of the ascidian *Polycarpa aurata*. At a concentration of 0.19 μmol litre⁻¹ it inhibits inosine monophosphate dehydrogenase. The fact that the inhibition can be eliminated by excess of dithiothreitol suggests that alkaloid **80** reacts with sulfhydryl groups of the enzyme.⁷⁸



73: R' = H, R'' = OMe;
74: R', R'' = O;
75: R', R'' = S;
76: R' = OMe, R'' = COOMe.



79: R = H, Me.

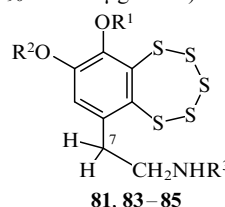


The tunicate *Lissoclinum perforatum* residing in North England contains 6,7-benzo-1,2,3,4,5-pentathiepanes with an annulated aromatic fragment: lissoclinotoxins A (**81**) and B (**82**) and isolissoclinotoxin A (**83**).^{79, 80} Lissoclinotoxin A **81** is a potent antimicrobial agent. Its activity against *Staphylococcus aureus*, *Streptococcus faecalis*, and *Citrobacter* sp. (MIC = 0.08–0.6 μg kg⁻¹) markedly exceeds that of the cephalosporine antibiotic cephotaxim. It also manifests sufficiently high activity against *E. coli*, *Salmonella* sp., *Proteus* sp., and *Pseudomonas aeruginosa*. Lissoclinotoxins A and B, especially compound **82** suppress ichthyopathogenic strains of *Aeromonas salmonicida* 643 and *Vibrio anguillarum* 5536.

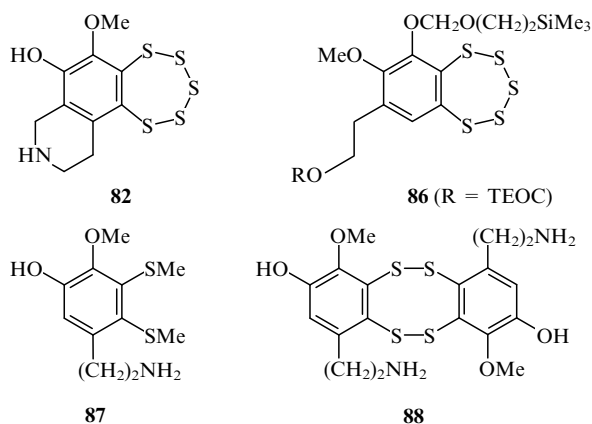
Lissoclinotoxin A demonstrates a rather high activity against the malaria pathogen *Plasmodium falciparum*, which is resistant to antimalarial drugs, such as mefloquine, galofantrine, and chloroquine. It exhibits the remarkable capacity to inhibit the growth of leukemia L 1210 cells when used at a concentration of 1 μg ml⁻¹. Lissoclinotoxin A manifests cytotoxic properties suppressing cell division in the sea urchin test.⁸⁰

The antitumor activity of varacin exceeds 100-fold that of 5-fluorouracil. Lissoclinotoxins C (**87**) and D (**88**), genetically related to lissoclinotoxin A, have been isolated from the tropical ascidia *Lissoclinum vareau*.⁸¹ These molecules are not diastereotopic. Lissoclinotoxin D, a dimeric derivative of lissoclinotoxin C, exerts fungicidal activity against *Candida albicans* at the same level as lissoclinotoxin A, whereas compound **88** is inactive.

The tropical ascidia *Lissoclinum vareau* contains varacin (**84**) possessing the fungicidal activity against *Candida albicans* and inhibiting the growth of human carcinoma HCT-116 cells ($IC_{90} = 0.05$ μg ml⁻¹).⁸¹

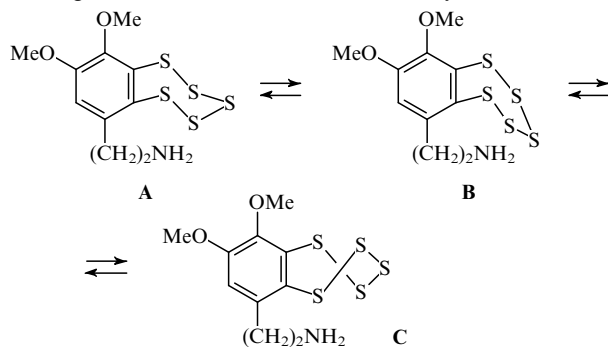


81: R¹ = Me, R² = R³ = H;
83: R¹ = R³ = H, R² = Me;
84: R¹ = R² = Me, R³ = H;
85: R¹ = R² = Me,
 R³ = COO(CH₂)₂SiMe₃ (TEOC).

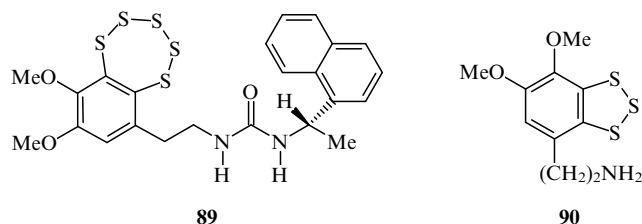


Lissoclinotoxins **81–83** and varacin **84** are the first presently known natural benzopentathiepine derivatives. Analysis of ^1H NMR spectra of compounds **81**, **84**, and their derivatives allowed one to conclude about the chirality of these molecules. Thus diastereotopicity of C(7)-methylene group protons has been observed in the spectrum of *N*-trimethylsilylethoxycarbonyl-varacin (*N*-TEOC-varacin) (**85**)⁸² and lissoclinotoxin A (**81**).⁸³ In compound **86**, the protons of the trimethylsilylethoxymethyl group are diastereotopic.

Thus, the interconversion of the benzopentathiepine system does not take place at room temperature. The inversion barrier in the lissoclinotoxin A molecule is 29 kcal mol⁻¹.⁸³ Calculations performed by the molecular mechanics method suggest that the chair (**A**) conformation for compound **84** is preferential as being energetically the most favourable. The second stable conformation, the energy of which is 8.7 kcal mol⁻¹ higher, is the 'twist' conformation **C**. The transition from the conformation **A** to the conformation **C** proceeds *via* the conformation **B**, the energy of which is higher than that of the conformation **A** by 34 kcal mol⁻¹.

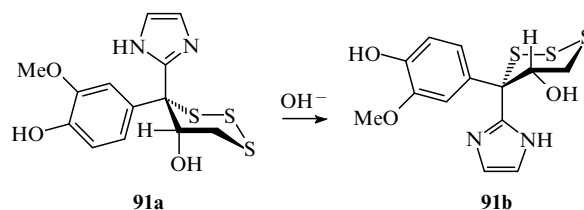


The ^1H NMR spectrum of a varacin derivative **89** contains double signals of the proton of the benzene ring and of both methoxy groups. This suggests the presence of two stereoisomers. A sample enriched with one isomer by 75% could be obtained by crystallisation.



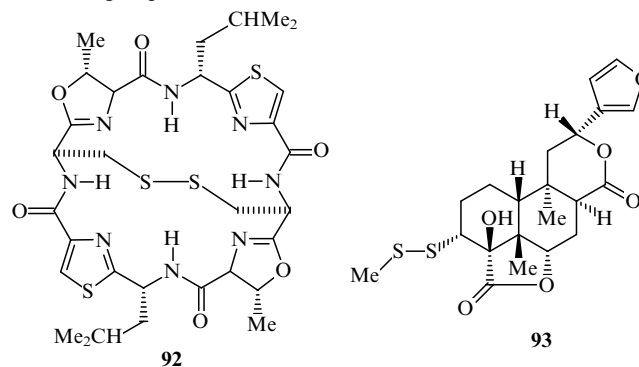
A benzotrithiane derivative **90** with fungicidal and antimicrobial activities against gram-positive and gram-negative bacteria (MIC = 0.1–0.6 $\mu\text{g ml}^{-1}$) and the fungi *Candida albicans* (40 $\mu\text{g ml}^{-1}$) and *Trichophyton mentagrophytes* (20 $\mu\text{g ml}^{-1}$) has been isolated from the tropical ascidian *Lissoclinum perforatum*.⁷⁹

The ascidia *Aplidium pliciferum* contains a trisulfide **91a** possessing antimicrobial, antitumour, and cytotoxic activities.⁸⁴ In alkaline media, the sulfur-containing ring is inverted to give a more stable diastereoisomer **91b** with an opposite configuration of the chiral carbon atom. Using NMR and molecular mechanics methods, it has been established that the trithiane ring in the epimer **91b** has a chair conformation in which the hydroxyl group occupies the equatorial position, whereas the imidazole ring is in the axial position. Based on the analysis of the NMR spectrum of the natural isomer **91a**, the chair conformation with the axial position of the hydroxyl group has been ascribed to the trithiane ring. Molecular modelling offers an alternative interpretation which entails rapid interconversion of two possible chair configurations. Both stereoisomers possess high biological activity: IC₅₀ values for their cytotoxic action against leukemia P 388 cells are 13 and 12 $\mu\text{g ml}^{-1}$, respectively.⁸⁴



An unusual cyclopeptide ulthiacyclamide (**92**) the molecule of which is built of two unusual amino acids is produced by the ascidian *Lissoclinum patella*. It is reported that compound **92** possesses strong cytotoxic activity and inhibits the growth of leukemia L1210 (at a concentration of 0.35 $\mu\text{g ml}^{-1}$) and human carcinoma CEM cells (at a concentration of 0.012 $\mu\text{g ml}^{-1}$).^{85–87}

The terpenoid disulfide menispermamide (**93**) has been isolated from the plant *Tinospora malabarica* of the *Menispermaceae* family.⁸⁸ This compound is the first representative of sulfur-containing terpenoids of the clerodane series.



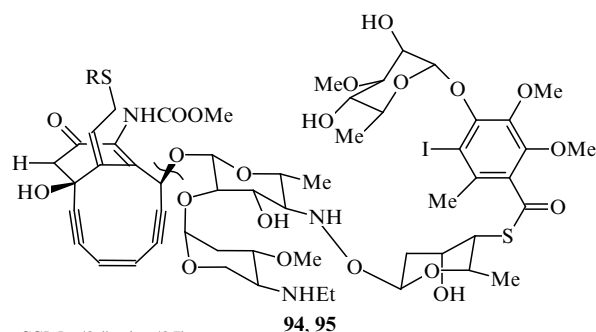
6. Antibiotics containing an enediyne fragment

Considerable interest in the past decade has been addressed to novel antibiotics, the aglycone fragment in which is an oxotrisulfide having the skeleton of a bicyclo[7.3.1]trideca-5-ene-3,7-diyne.

Thus calichemycin γ_1 (**94**) produced by the culture of *Microspora echinospora* possesses extraordinary antitumour activity, which exceeds 4000-fold that of adriamycin, one of the best modern cancerostatic agents.^{89–95}

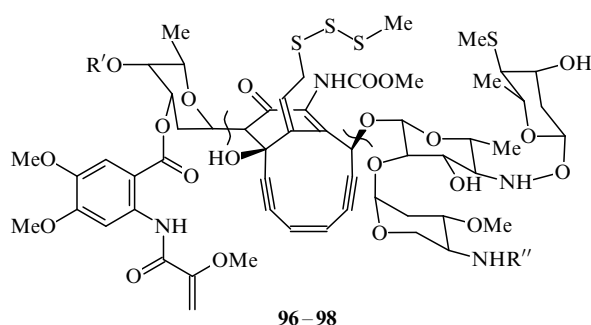
The antitumour and cytotoxic activities of calichemycin γ_1 and its synthetic analogue, calichemycin θ_1 (**95**)⁹⁵ in which the trisulfide fragment had been replaced by the etylthio group, have been studied with respect to a vast variety of cells beginning with the relatively stable melanoma SK MEL 28 cells (IC₅₀ = 1.6 $\times 10^{-9}$ M) and ending up with highly sensitive leukemia MOLT-4 cells (IC₅₀ = 10⁻¹² M).

Esperamycins A₁, A₂ and A_{1b} (compounds **96–98**, respectively) also appear to be potent cancerostatic agents.^{96–98} These strikingly remarkable molecules are unique in all the elements of



R = SSMe (**94**), Ac (**95**).

their structure. Thus the structure of the carbohydrate skeleton and of the aglycone of the antibiotics has no precedents in the chemistry of natural compounds. Carbohydrate fragments involve rare thio- and amino sugars linked through a unique, hydroxylamine bond. The structures of the polysubstituted benzoic acids deserve individual mention.

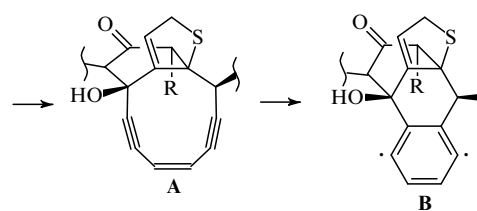
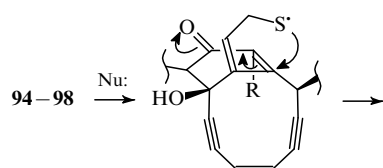


96-98

96: R' = H, R'' = Pr^t; **97**: R' = Ac, R'' = Bu^t; **98**: R' = H, R'' = Et.

The mechanism of the anticarcinogenic effect of enediyne antibiotics entails active involvement of the trisulfide fragment. At the first stage, the enediyne system forms associates with double-stranded DNA; the complex formation affects predominantly the DNA region enriched with pyrimidine bases. Using ¹H NMR technique, the formation of a 1 : 1 complex with a duplex containing the A-C-C-T fragment, and of a 1 : 1 complex with the T-T-T-T fragment has been established. It is reasoned that the coordination with the pyrimidine-containing fragments is conformationally more favourable than that with the purine fragments.⁹⁹

An important role in the binding to DNA is ascribed to the side chain of enediyne antibiotics **94-98**. The analysis of six models of calicheamicin complex formation has led to a conclusion that the model that involves the binding of rhamnose, thiobenzoic acid, and the thio sugar to the DNA region 5'-T-C-C-T/3'-A-G-G-A is more preferable.^{100, 101} Cleavage of the trisulfide fragment is crucial for the stage of conjugated addition of the thiol residue according to the anti-Bredt rule. Bioreduction to the dihydrothiophene intermediate **A** initiates the key Bergman cyclisation, eventually resulting in the conversion of enediyne into diyl (**A** → **B**). Diyl **B** is responsible for DNA cleavage that begins with hydrogen detachment from the 2-deoxyribose residue.^{102, 103} The mechanism of activation of calicheamicin θ₁ (**95**) is different in that an oxygen-, sulfur-, or nitrogen-containing nucleophile is used as an activator, whereas enediynes **94** and **96-98** are activated by thiols.⁹⁵ The problem of complex formation of calicheamicin γ₁ is also discussed in a paper by Mah *et al.*,¹⁰⁴ which also gives a detailed list of references.

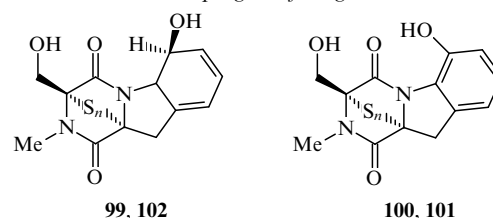


R = NHCOOMe.

7. Sulfur-containing piperazinediones

Let us now dwell on the characteristics of fungal metabolites that have a polythiapiperazinedione fragment in their structure. The chemistry and toxicology of these compounds and the literature coverage of up to 1980 have been reviewed.^{105, 106}

Glyotoxin (**99**) produced by *Aspergillus fumigatus*, *Gliocladium fimbriatum*, and *Penicillium terlikowski* is highly toxic against homoiothermal organisms.¹⁰⁷⁻¹⁰⁹ Dehydroglyotoxin (**100**) and the corresponding trisulfide (**101**) have been isolated from the metabolites of the fungus *Pithomyces chartarum*.^{110, 111} The tetrasulfide (**102**) termed glyotoxin G has been identified as a minor metabolite of *Aspergillus fumigatus*.^{109, 112}

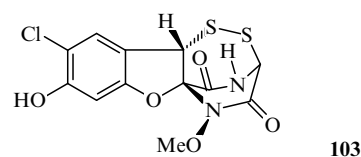


99, 102

100, 101

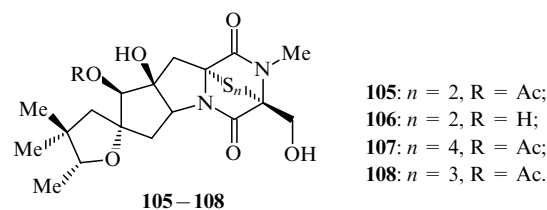
n = 2 (**99**, **100**), 3 (**101**), 4 (**102**).

The fungus *Aspergillus tamari* produces a chlorophenolic metabolite aspirochlorine (**103**).^{113, 114} Aspirochlorine (**103**) is highly active *in vitro* against gram-positive bacteria and fungi (IC₅₀ = 0.1–50 mg kg⁻¹); however, in contrast with the epidi-thiapiperazine-2,5-diones (**99-102**) described above, it exhibits only slight fungicidal and antiviral activities.¹¹⁵ The above-mentioned differences in biological activity can be due to differences in the strain of bicyclo[2.2.2] systems in **99** and **100** and bicyclo[3.2.2] systems in **103**. Like glyotoxins **99-102**, aspirochlorine is a strong immunosuppressor and inhibits phagocytosis.¹¹⁶



103

A phytopathogen *Phoma lingam* affecting rape and cabbage produces several toxins. One of them, phomalirazine (**104**), is produced exclusively by this fungus. The other two compounds, sirodesmins PL (**105**) and H (**106**), are also metabolites of the fungus *Sirodesmium diversum*.^{117, 118} The latter also produces sirodesmins B (**107**) and C (**108**).



105-108

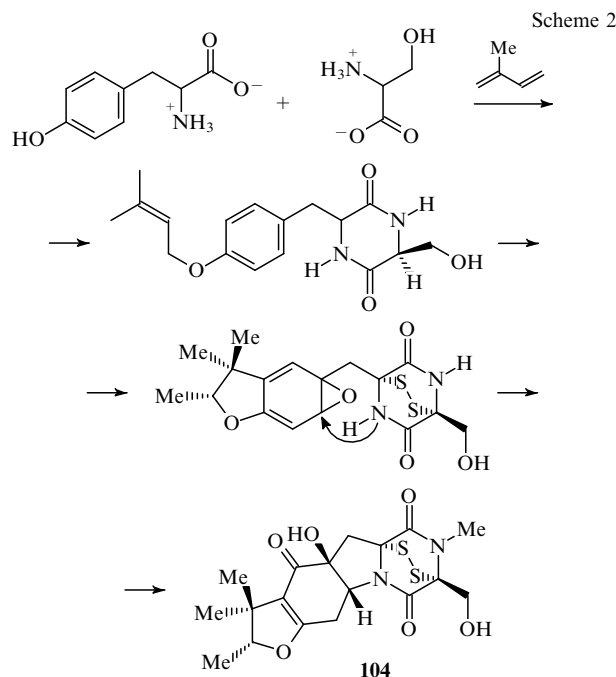
105: n = 2, R = Ac;

106: n = 2, R = H;

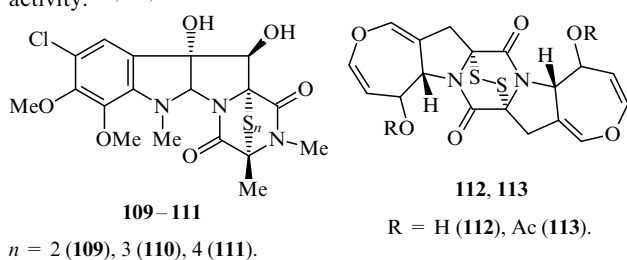
107: n = 4, R = Ac;

108: n = 3, R = Ac.

Sirodesmins possess antiviral activity against *Vaccinia*, *Herpes*, and Newcastle disease viruses.¹¹⁹ Phomalirazine is the precursor of sirodesmins. Its biosynthesis begins with tyrosine and serine and involves isoprene (Scheme 2).¹¹⁸



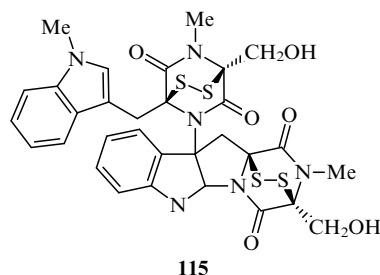
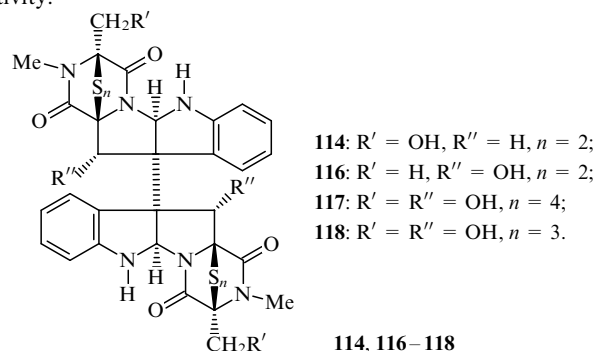
Sporidesmins A, E, and G (**109–111**) isolated from the culture of the fungus *Phthomyces chartarum* possess marked antibiotic activity.^{108, 111, 120}



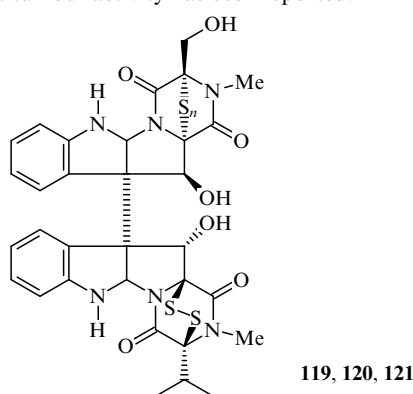
Metabolites of the fungus *Arachniotus aureus* have been found to contain dithiapiperazinedione aranotine (**112**) and its diacetate **113**, which exhibit *in vitro* and *in vivo* antiviral effects.^{121, 122} The latter is also produced by *Aspergillus*.¹²³

Chetocine (**114**)¹⁰⁸ and chetomine (**115**) are metabolites of the fungi *Chaetomium minutum* and *Ch. cochliodes*.¹²⁴ The latter compound is highly toxic against homoiothermal organisms. High antibacterial activity has been established for chetocine **114** (MIC for *Staphylococcus aureus* is $0.01–0.001$ mg ml⁻¹), and its cytotoxicity index (IC₅₀) with respect to P-815 tumour cells is 0.038 mg litre⁻¹.

Fungi *Verticillium* produce the antibiotics verticillins A–C (**116–118**), which suppress gram-positive and gram-negative bacteria and inhibit the growth of some other fungi and cancer cells^{125, 126} (the cytotoxic effect, ED₅₀, of compounds **116** and **117** with respect to HeLa cells is 0.2 µg ml⁻¹). It is interesting to note that polythiapiperazinediones **114–118** are devoid of antiviral activity.¹²⁷



The structure of leptosines A–C (**119–121**), the secondary metabolites of the fungi *Leptosphaeria* sp. isolated from the sea alga *Sargassum forfile* has been recently established. Their high antitumour activity has been reported.^{128, 129}

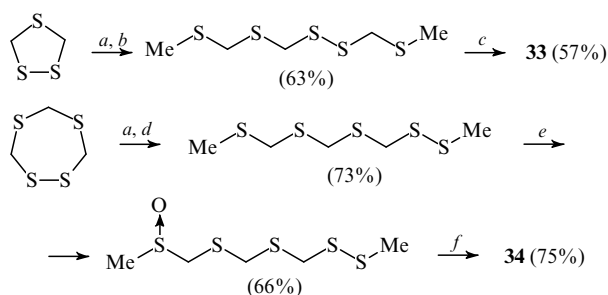


III. Synthesis of natural di- and poly-sulfides and their analogues

As can be seen from the presented data, naturally occurring polysulfides present special interest by virtue of their unusual structures and remarkable physiological activity. The latter fact has stimulated studies aimed at total synthesis of these compounds and their structural analogues.

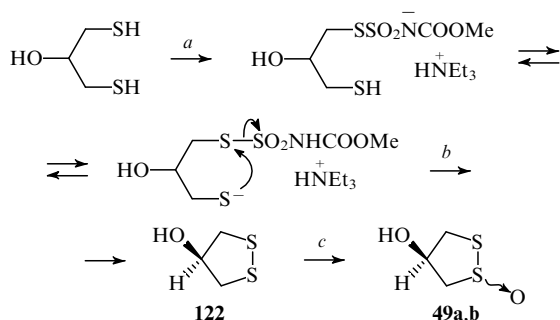
Syntheses of the biologically active linear polysulfides, viz., 2,4,5,7,9-pentathiadecane-2,2,9,9-tetraoxide (**33**), 2,3,5,7,9-pentathiadecane-9,9-dioxide (**34**), and 2,4,5,7-tetrathiaoctane-2,2-dioxide isolated from the plant *Tulbaghia violacea*¹³⁰ have been carried out starting from the corresponding polythiacyclanes. The key stage in these syntheses is the nucleophilic ring-opening of 1,2,4-trithiolane (**37**), 1,2,4,6-tetrathiepane (**38**), and 2,4,5,7-tetrathiaoctane with MeLi, trapping of thiolate ions formed by electrophiles, and subsequent regio-specific oxidation of intermediate penta- or tetra-sulfides with KMnO₄ in a mixture with Zn(OAc)₂ or FeCl₃ in order to prevent the cleavage of the final product with a base formed in the oxidation.¹³¹ The synthesis of polysulfides **33** and **34** is shown in Scheme 3.

Scheme 3



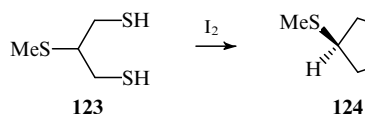
(a) MeLi; (b) MeSCH₂SSO₂Me; (c) KMnO₄, Zn(OAc)₂, MgSO₄, Me₂CO; (d) MeSSO₂Me; (e) H₂O₂, AcOH; (f) KMnO₄, MgSO₄, Me₂CO.

Much attention has been given to the synthesis of natural 1,2-dithiolane derivatives. The key problem in this synthesis is the formation of the dithiolane ring. To this end, reactions of 1,3-diol, ditosylate, dithiol, and dihalide derivatives with sodium disulfide, thiourea, thioacetic acid, or α -toluenethiol were employed. The use of (*N*-methoxycarbonyl-sulfamoyl)triethylammonium hydroxide for the formation of the disulfide bond has been described.⁴³ The interaction of the latter with 1,3-dimercaptopropan-2-ol gives 4-hydroxy-1,2-dithiolane (**122**) the oxidation of which with hydrogen peroxide results in a mixture of diastereoisomeric sulfoxides **49a,b** in a 4 : 1 ratio.



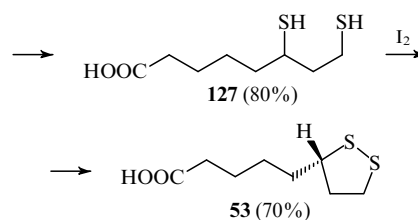
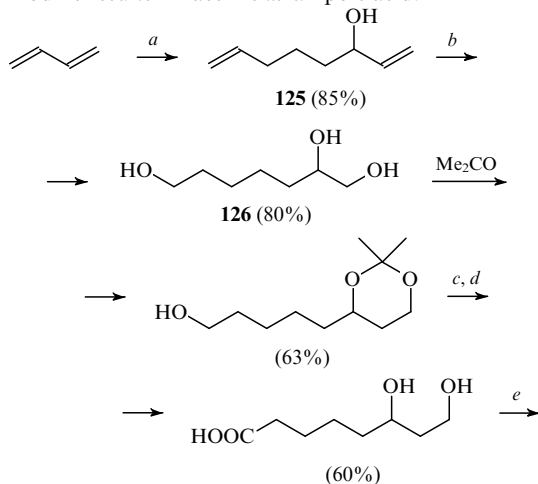
(a) $\text{Et}_3\text{N}^+\text{SO}_2\text{N}^-\text{COOMe}$, CHCl_3 , 20 °C; (b) 0.5 N NaOH;
(c) H_2O_2 , CHCl_3 , MeCN, 20 °C, 48 h.

The direct oxidation of 2-methylthiopropene-1,3-dithiol (**123**) with iodine has been used in the synthesis of 4-methylthio-1,2-dithiolane (**124**) in 78% yield. The latter was isolated together with trithiane **48** from the green alga *Chara globularis*.⁴¹



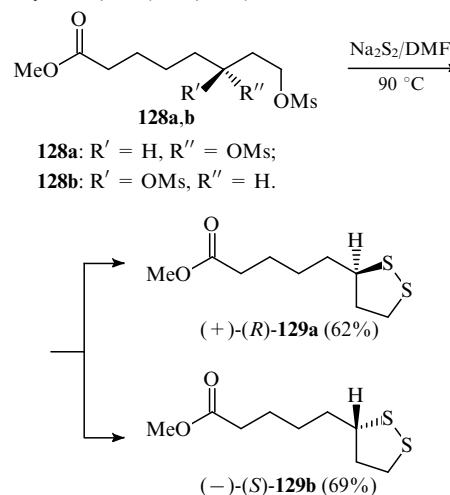
It is interesting to note that the reaction of dithiol **123** with SCl_2 gives a mixture of cyclic sulfides **124** and **48** in a 1 : 1 ratio.¹³²

The main problem in the synthesis of lipoic acid (**53**) and its derivatives is the introduction of the side chain. A simple synthesis employing octa-1,7-dien-3-ol (**125**), which is the product of butadiene telomerisation with water¹³³ in the presence of palladium complexes, has been described.¹³⁴ The hydroboration of octadienol **125** with borane results in the triol (**126**); isopropylidenation of the 1,3-diol, oxidation of the free terminal hydroxy group at C(8) with the Jones reagent, methylation, deprotection, and the reaction with thiourea give the dithiol (**127**). Its oxidation with iodine results in racemic *dl*- α -lipoic acid.

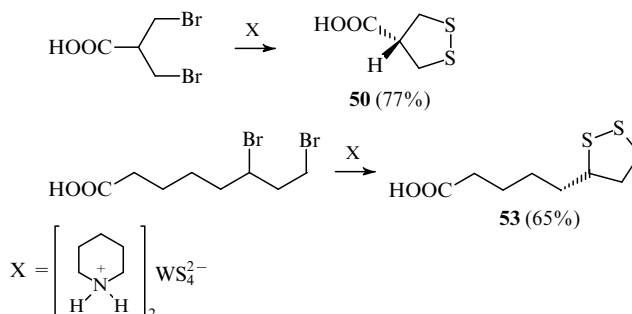


(a) $\text{PdCl}_2(\text{PPh}_3)_2$, H_2O , KOH; (b) B_2H_6 , THF, H_2O_2 –NaOH; (c) CrO_3 – H_2SO_4 , CH_2N_2 ; (d) H_2SO_4 –MeOH; (e) $(\text{NH}_4)_2\text{CS}$ –57% HI–NaOH.

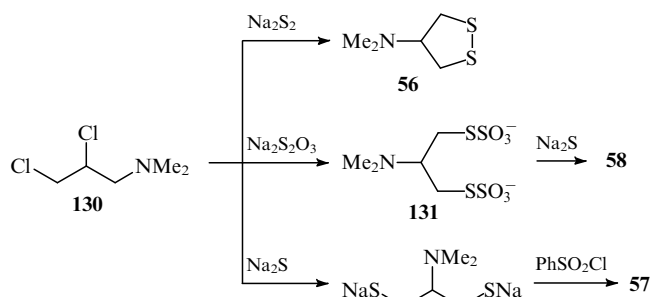
More often, nucleophilic substitution in the corresponding 1,3-dihalides or 1,3-disulfonates is used in the synthesis of 1,2-dithiolanes. For example, methyl esters of (+)-(*R*)- and (–)-(*S*)-lipoic acids **129a,b** have been synthesised by the reaction of dimesylates (**128a**) or (**128b**) with sodium disulfide.¹³⁵



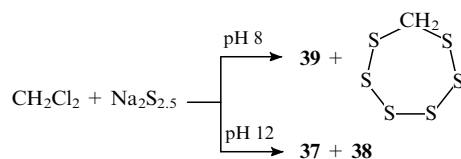
Good results in the synthesis of cyclic disulfides have been obtained with piperidinium tetrathiatungstate.¹³⁶ The latter reacts with dihalides to give the corresponding disulfides in a good yield and under mild conditions (25–40 °C, 4–5 h, DMF). This method has been used in the synthesis of (+)-lipoic acid **53** and asparagusic acid **50**.



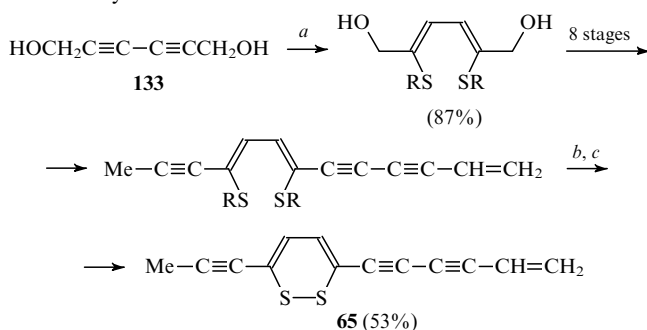
The synthesis of nereistoxin (**56**) and its analogues that are used as insecticides has a number of specific features. The dihalogenamine **130**, obtained by chlorination of allyldimethylamine is the starting compound. Under the action of sulfur nucleophiles, the amine **130** is rearranged *via* an intermediate sulfonium ion into derivatives of 1,3-dithio-substituted 2-dimethylaminopropanes. The reaction of dihalogenamine **130** with Na_2S_2 directly results in nereistoxin **56**,¹³⁷ whereas its interaction with Na_2S and then with benzenesulfonylchloride gives bensultap (**57**).¹³⁸ The treatment of 1-dimethylamino-2,3-dichloropropane (**130**) with sodium thiosulfate gives the compound **131**, which gives the trisulfide **58** upon treatment with Na_2S .⁴⁹



Nucleophilic substitution underlies the synthesis of the pentasulfide lenthionine (**39**), trisulfide **37**, and the tetrasulfide **38** from the readily available CH_2Cl_2 and $\text{Na}_2\text{S}_{2.5}$.¹³⁹



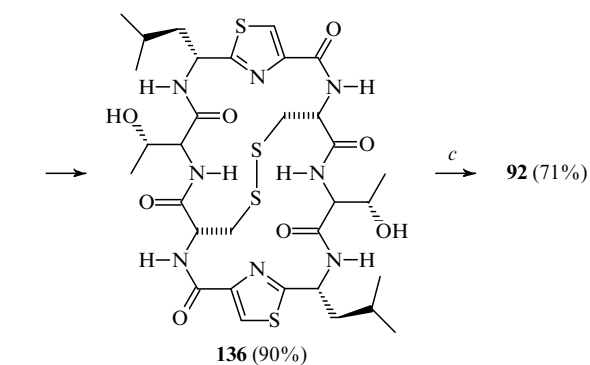
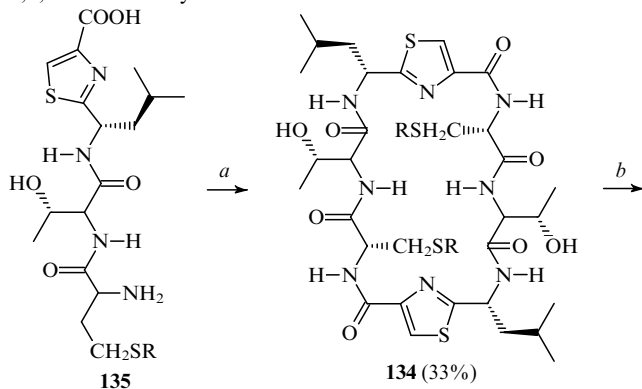
The synthesis of thiarubrin A (**65**) from hexa-2,4-diyne-1,6-diol (**133**) involves 12 steps. The use of 2-(trimethylsilyl)ethanethiol as a protecting group in the formation of the 1,2-dithiylne is noteworthy.⁵⁸



R = $\text{Me}_3\text{SiCH}_2\text{CH}_2$.

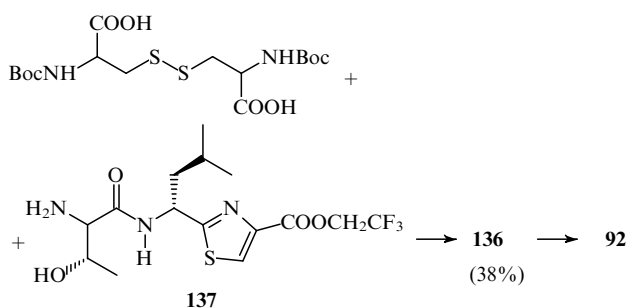
(a) $\text{Me}_3\text{Si}(\text{CH}_2)_2\text{SH}$, KOH – DMF, 20 °C; (b) Bu_4NF , molecular sieves 3 Å; (c) I_2 , 20 °C, 30 min.

The formation of the disulfide bond upon oxidation of dithiols or their derivatives with iodine has been used in syntheses of structurally complex metabolites. Thus in the synthesis of ultracyclamide (**92**) it is the *S*-acetamidomethyl derivative **134** formed upon cyclodimerisation of the corresponding *S*-acetamidomethyl tripeptide (**135**) effected by diphenylphosphorazidate (DPPA) and triethylamine that undergoes oxidation with iodine.¹⁴⁰ The oxazole ring in the molecule **92** is formed by treatment of the intermediate disulfide **136** with an excess of thionyl chloride. This synthesis of a cytotoxin **92** competes favourably (as regards the overall yield and the number of stages) with the synthesis involving bis-cyclisation of cystine with the 2,2,2-trifluoroethyl ester **137**.¹⁴¹

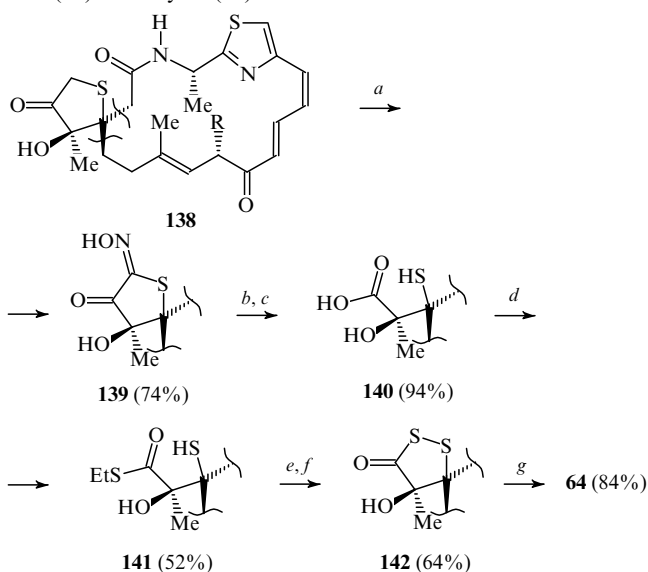


R = CH_2NHCOMe .

(a) DPPA – Et_3N , DMF; (b) I_2 , MeOH; (c) SOCl_2 , 0 °C, 17 h.



An original method for the introduction of a 1,2-dithiolan-3-one fragment as a spirofusion with an 18-membered lactam containing a thiazole ring has been offered in Ref.¹⁴². The nitrosylation of thiolanone **138** gives the oxime **139**. Subsequent protection of the keto group of the dienone fragment as the *O*-methyloxime followed by Beckmann rearrangement under the action of 2,6-dimethylbenzoyl chloride results in a mercapto acid **140**, which was further converted into the thioester **141**. Treatment of the latter with sodium hydrogen sulfide and iodine with subsequent deprotection are followed by cyclisation leading to (*S*)-deoxyunamycin (**142**), which is stereoselectively oxidised into (+)-leinamycin (**64**).

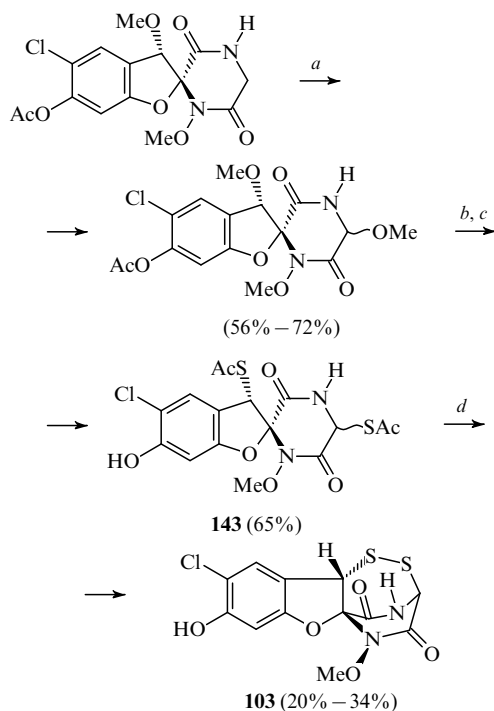


R = OCH_2OMe .

(a) Am^iONO , NaOMe , 23 °C, 1.5 h; (b) $\text{MeONH}_2 \cdot \text{HCl}$, Py; (c) 2,6- $\text{Me}_2\text{C}_6\text{H}_3\text{COCl}$, Py; (d) EtSH , THF, 20 °C, 20 min; (e) NaSH , THF, I_2 , 10 min; (f) 33% HCHO , 3 N HCl , Me_2CO ; (g) 3- $\text{ClC}_6\text{H}_4\text{CO}_3\text{H}$, THF, 0 °C, 45 min.

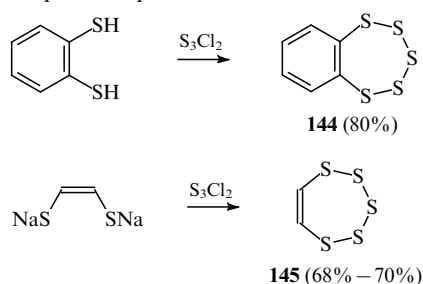
The total synthesis of the disulfide antibiotic aspirochlorine (**103**) from 4-chlororesorcinol includes 14 stages. The most notable are the final steps shown in Scheme 4. The methoxy group is introduced into the piperazinedione ring by treatment with *tert*-butyl hypochlorite in methanol in the presence of sodium methoxide. This is followed by substitution of two methoxy groups for the acetylthio groups under the action of thioacetic acid in the presence of boron trifluoride etherate. And, finally, the closure of the disulfide bridge is performed by treatment of bithioacetate **143** with *O*-methylhydroxylamine and camphorsulphonic acid.¹¹⁴

Scheme 4

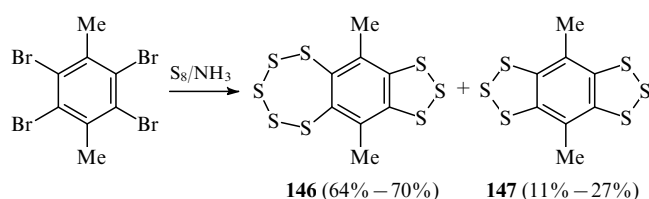


(a) Bu^tOCl , NaOMe ; (b) NaOEt – EtOH ; (c) AcSH , $\text{BF}_3 \cdot \text{Et}_2\text{O}$; (d) MeONH_2 , *d*-camphorsulphonic acid, THF, 23 °C.

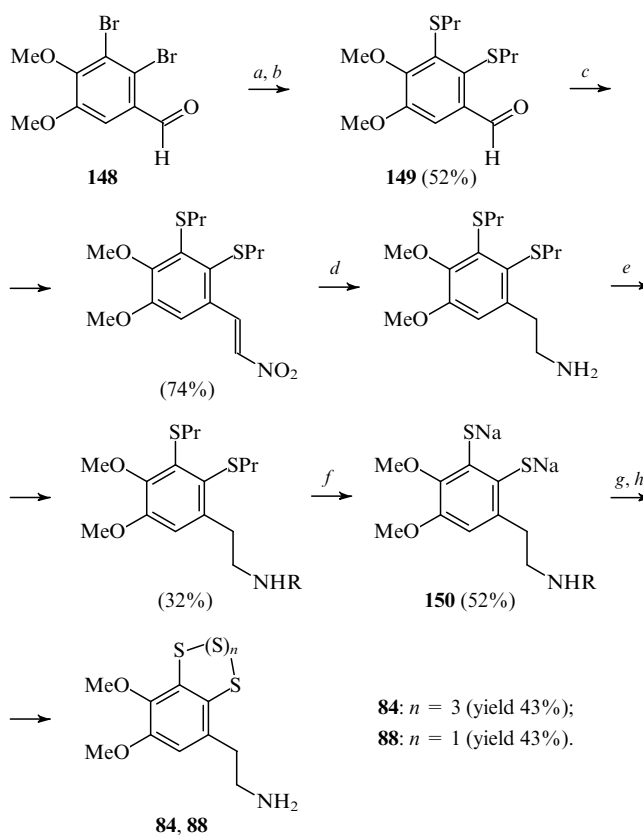
Considerable attention has been paid to the synthesis of benzopentathiepine **144** and its analogue **145**. Benzopentathiepine is formed by treatment of benzene-1,2-dithiol with S_3Cl_2 in ether, the yield being up to 80%.^{143, 144} An analogous scheme is used to obtain pentathiepine **145**.



An interesting method for the introduction of a pentathiepine fragment¹⁴⁵ is based on the reaction of aromatic *o*-dibromides with sulfur in liquid ammonia. In this case, trisulfide derivatives **147** are formed along with the main reaction product **146**.



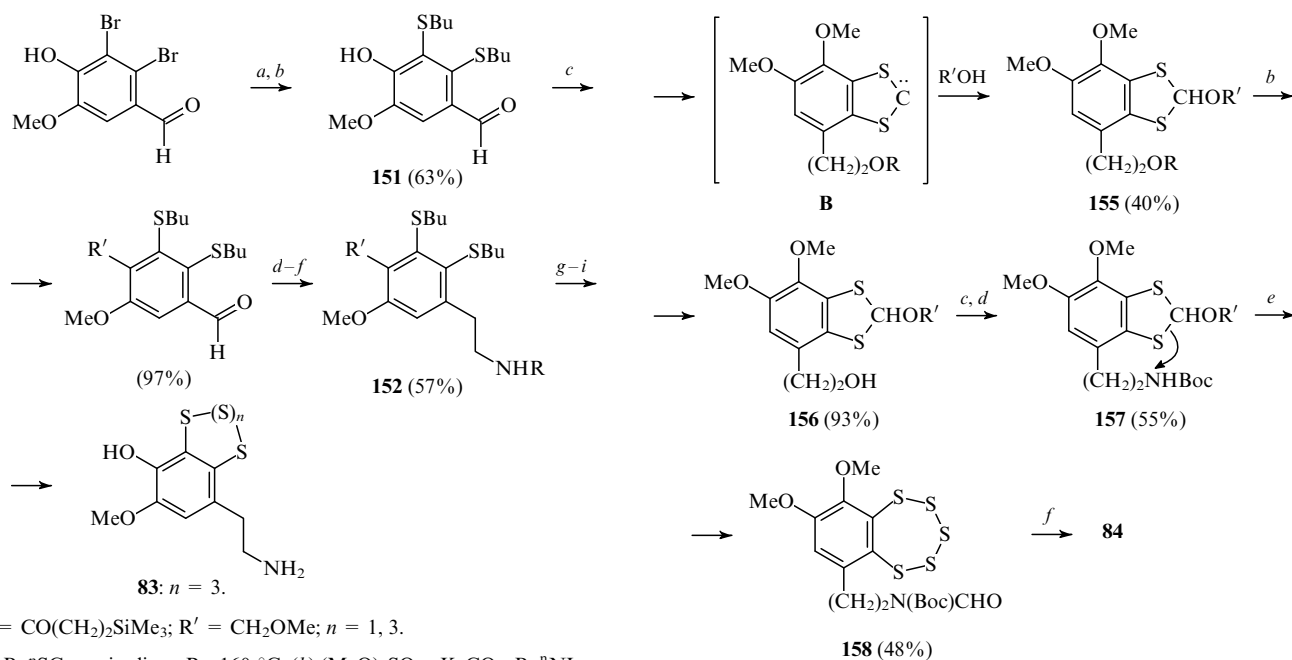
The interest in the synthesis of varacin (**84**) and lissoclinotoxins (**81**–**83**) is explained primarily by their valuable biological activity. Schemes of total synthesis of varacin (**84**) and isolissoclinotoxin (**83**) from vanillin in which the pentasulfide fragment was prepared from *o*-dimercaptobenzenes are described. Thus the treatment of 2,3-dibromoveratric aldehyde **148**, which was obtained from vanillin, with copper propanethiolate and remethylation of hydroxy groups resulting from partial demethylation of methoxy groups gave the dipropylthio derivative **149**.¹⁴⁶ This was followed by the reaction of **149** with nitromethane, reduction of the nitro group with lithium aluminium hydride, and protection of the resulting amino group. Splitting of the thioester groups with sodium in ammonia and the reaction of disodium dithiolate **150** with S_2Cl_2 gives a mixture of benzotriothiole and benzopentathiepine **84** in a total yield of 86%. The final stage is non-selective, because trisulfide **88** is formed along with varacin **84** in a 1 : 1 ratio.



R = TEOC.

(a) PrSCu , quinoline–Py, 160 °C; (b) $(\text{MeO})_2\text{SO}_2$ – K_2CO_3 , Bu_4NI , CH_2Cl_2 – H_2O ; (c) MeNO_2 , $\text{NH}_4\text{OAc}/\text{AcOH}$, 23 °C; (d) LiAlH_4 , THF, 65 °C, 25 min; (e) 4- $\text{NO}_2\text{C}_6\text{H}_4\text{OR}$, Et_3N – CH_2Cl_2 ; (f) Na/NH_3 ; (g) S_2Cl_2 –THF, 25 °C, 45 min; (h) CF_3COOH , CHCl_3 , 20 °C, 50 min.

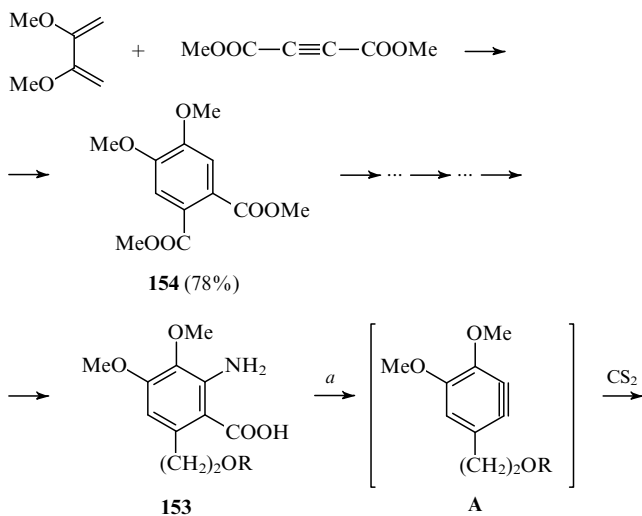
The key step in the synthesis of isolissoclinotoxin A (**83**) is the reaction of 5,6-dibromovanillin with copper butanethiolate resulting in the dithioether **151**.¹⁴⁷ The protection of the phenolic hydroxyl at position 4 with methoxymethyl chloride and subsequent introduction of the nitrogen-containing substituent according to the aforementioned reaction sequence give compound **152**. Reduction of the *o*-butylthio groups with sodium in ammonia and subsequent treatment of the dithiolate anion with S_2Cl_2 give a mixture of penta- and tri-sulfides in a 2.4 : 1 ratio.



$R = \text{CO}(\text{CH}_2)_2\text{SiMe}_3$; $R' = \text{CH}_2\text{OMe}$; $n = 1, 3$.

(a) Bu^nSCu , quinoline–Py, 160 °C; (b) $(\text{MeO})_2\text{SO}_2 - \text{K}_2\text{CO}_3$, Bu_4^nNI , $\text{CH}_2\text{Cl}_2 - \text{H}_2\text{O}$; (c) CH_2ClOMe , Pr_2NEt , CH_2Cl_2 , 23 °C; (d) MeNO_2 , $\text{NH}_4\text{OAc}/\text{AcOH}$; (e) LiAlH_4 , THF, 65 °C, 25 min; (f) $4\text{-NO}_2\text{C}_6\text{H}_4\text{OR}$, $\text{Et}_3\text{N} - \text{CH}_2\text{Cl}_2$; (g) Na/NH_3 (yield 50%); (h) $\text{S}_2\text{Cl}_2 - \text{THF}$, 25 °C, 45 min (yield 67%); (i) CF_3COOH , CHCl_3 , 20 °C, 50 min (yield 86%);

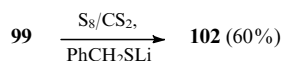
In the scheme of the synthesis of varacin (**84**),¹⁴⁸ of special note is the approach allowing selective introduction of a pentasulfide fragment. The initial product is the substituted anthranilic acid **153** which is readily formed from diester **154**. Treatment of the acid **153** with isopentyl nitrite in the presence of carbonic sulfide and isopentyl alcohol gave cyclic dithioether **155** formed *via* intermediates **A** and **B**. In order to introduce the nitrogen-containing substituent, silyl protection was removed and the alcohol formed **156** was introduced into the reaction with phthalimide. Splitting of the phthaloyl protection by hydrazinolysis resulted in a free amino group further protected as a BOC derivative to give the compound **157**. Treatment of the latter with S_2Cl_2 cleaves the orthoester and yields the pentathiepine ring. It is of note that the transfer of the formyl residue from the sulfur-containing to the nitrogen-containing substituent occurs in the course of pentathiepine **158** formation.



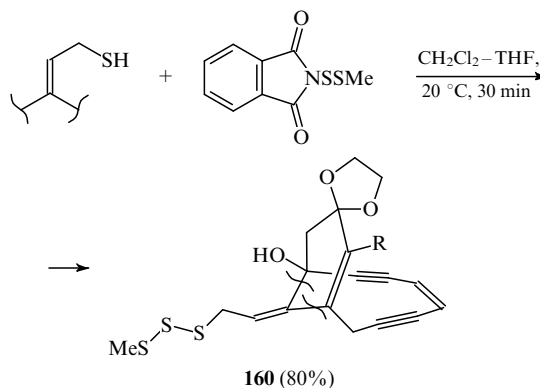
$R = \text{Bu}^t\text{Ph}_2\text{Si}$; $R' = \text{Penti}$.

(a) Pent^tONO , PentOH , CS_2 , CH_2Cl_2 , 75 °C, 30 min; (b) Bu_4NF , THF, 23 °C, 30 min; (c) phthalimide, $\text{EtOOCN} = \text{NCOOEt}$, PPh_3 , THF, 25 °C, 27 h; (d) N_2H_4 , EtOH , $(\text{Boc})_2\text{O}$, $4\text{-Me}_2\text{NC}_5\text{H}_4\text{N}$, CH_2Cl_2 ; (e) S_2Cl_2 , THF, 20 °C, 25 min; (f) $\text{HCl} - \text{MeOH}$.

The conversion of the easily accessible disulfide glyotoxin **99** into the tetrasulfide glyotoxin **G 102** was effected by treatment with sulfur and lithium α -toluenethiolate (0.1 equivalent) in CS_2 .¹¹²



An increasing number of papers have been dedicated to the synthesis of calicheamicin (**94**) and esperamycins (**96–98**). The introduction of the trisulfide fragment is not a challenging task. For example, the synthesis of a model compound **160** from the corresponding thiol was carried out by a standard procedure.¹⁴⁹



$R = \text{NHCOOMe}$.

The references^{150–156} are related to the total synthesis of sulfur-containing enediyne antibiotics and their fragments.

IV. Conclusion

As can be seen from the data presented, the natural polysulfides constitute a promising group of low-molecular-weight bioregulators. The chemistry of many of them is of substantial interest.

Thus the long-standing controversies about the nature of the biologically active substances of onion and garlic have been

resolved only very recently and required the use of sophisticated analytical procedures. One cannot but mention in this connection the promising studies dedicated to the modelling of structures of biologically active components of garlic.

There is no doubt that the knowledge of the mechanisms of action of unique trisulfide enediyne antibiotics will open up new routes in the search for inhibitors of growth of malignant tumours.

Some polysulfides of marine organisms draw attention with a combination of high biological activity and relatively simple structures. Taking into account the present-day level of organic synthesis, it may be thought that further development of technological methods for the synthesis of the most promising natural compounds and their active analogues is quite a realistic task. In this respect an appropriate example is the organisation of the large-scale manufacture of a selective insecticide bensultap, an analogue of the natural insecticide nereistoxin.

It is thought that keen attention of synthetic chemists will be drawn to natural aromatic polysulfides and dithiin derivatives possessing high antitumour activity.

Thus the chemistry of natural polysulfides offers a vast field for specialists in organic synthesis, who are interested in the synthesis of complex structures, as well as for all those who are engaged in the design of biologically active compounds.

The material presented herein prompts a conclusion that further developments in the field of chemistry and biochemistry of natural polysulfides and their analogues will have consequences which are valuable from the practical point of view for medicine and agriculture. Also of significance is the acquisition of fundamental knowledge of the reactivity and stereochemistry of sulfur-containing cyclic systems.

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Nitrobutadienes and their halogen derivatives: synthesis and reactions

R V Kaberdin, V I Potkin, V A Zapol'skii

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Abstract. The main methods of the synthesis of nitrobutadienes and their halogen derivatives, which are multipurpose electrophiles, are surveyed. The literature data on their chemical transformations are generalised, the possibilities for the preparation of new polyfunctional derivatives of different classes on the basis of nitro- and halo-nitrobutadienes that have been inaccessible earlier are demonstrated. The bibliography includes 112 references.

I. Introduction

The chemistry of nitro compounds has been intensively studied during the last 20–25 years. Since 1970, many scientific papers, monographs,^{1–3} and reviews^{4–18} on the synthesis and the properties of these compounds have been published.

The interest in nitro compounds is primarily due to the possibilities of their application as unique intermediate products for the synthesis of various organic compounds. It should be noted that at present most attention is attracted to aliphatic nitro compounds. Thus, a review⁴ that first suggested the versatility and importance of aliphatic nitro compounds in organic synthesis appeared back in 1979. The results of subsequent studies in this direction (see for instance^{5,6}) have confirmed the importance of new investigations in the chemistry of nitro compounds of the aliphatic series.

At present, much attention is paid to the synthesis and the properties of nitro-alkenes and -alkadienes. Studies along the first direction are rather diverse and mostly concern such specific questions as the synthesis of nitrogen-containing heterocycles involving O and N atoms of the alkene nitro group,⁹ methods of synthesis and reactions of allylic nitro compounds and their derivatives,¹⁵ and others.^{12,16}

Recently interest increased in nitrobutadienes, and especially their halogen derivatives. These highly reactive substances were used to develop preparative methods for the synthesis of complex polyfunctional derivatives of different classes, that have been virtually inaccessible before. Thus an original method for the

synthesis of a valuable amino acid, lysine, from 1-nitrobuta-1,3-diene has been proposed. A convenient route for building of isothiazole cycle from 2-nitropentachlorobuta-1,3-diene and sulfur has been developed. Halogen derivatives of nitrobutadienes are suitable model objects for elucidation of the features of nucleophilic vinylic substitution ($S_N\text{Vin}$).

The publications that cover this subject, published before 1985, have been only partially discussed in monographs^{1–3} and a review.⁸ We have surveyed and systematised the results of investigations performed during the last two decades in the chemistry of nitrobutadienes and their halogen derivatives.

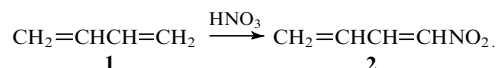
II. Synthesis of nitrobutadienes and their halogen derivatives

Basically, two main methods for the synthesis of nitrobutadienes including their halogen derivatives are used: (1) the direct nitration of butadiene and its derivatives by different nitrating agents; (2) the synthesis from more complex aliphatic nitrocompounds by elimination of different molecules (hydrogen halides, acetic acid, *etc.*). In some cases the formation of different geometric isomers of the nitro-substituted butadienes is possible. However, the configuration and the ratio between *E*- and *Z*-isomers have not been determined for all the halogenonitrobutadienes synthesised, therefore, we specify the isomeric form only if it is given in the literature, cited.

1. Preparation of nitrobutadienes and their halogen derivatives by nitration of dienes

a. Synthesis of mononitrobutadienes

The direct nitration of butadiene (**1**) by nitric acid results in 1-nitrobutadiene (**2**).^{19,20}



The conditions of this and other nitration reactions are summarised in Table 1. Dinitrogen tetroxide, dinitrogen pentoxide, and N_2O_4 in an oxygen flow can be used as the nitration agents in reaction with butadiene.^{8,21,22} However, the formation of nitrobutadienes was not observed in these cases, the reactions lead to the products of addition of NO_2 and ONO_2 to the diene **1**: 1,4-dinitrobut-2-ene (**3**), 4-nitrobut-2-enylnitrate (**4**) or 1-nitrobut-3-enyl-2-nitrate (**5**). The latter were used for the synthesis of nitrobutadiene **2** (see Section II.2).

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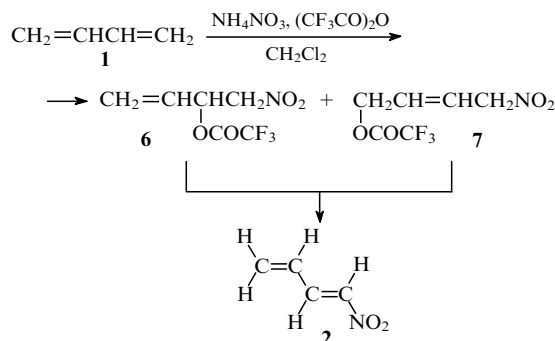
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Table 1. Synthesis of nitrobutadienes and their halogen derivatives by nitration of the butadienes.

Starting diene	Nitrating reagent	$T/^{\circ}\text{C}$	Nitrobutadiene	Yield (%)	Ref.
$\text{CH}_2=\text{CHCH}=\text{CH}_2$ 1	Fuming HNO_3	—	$\text{CH}_2=\text{CHCH}=\text{CHNO}_2$ 2	—	19, 20
$\text{CH}_2=\text{CHCH}=\text{CH}_2$ 1	$\text{CF}_3\text{COONO}_2$	—	$\text{CH}_2=\text{CHCH}=\text{CHNO}_2$ 2	89	23, 24
$\text{Cl}_2\text{C}=\text{CClCH}=\text{CCl}_2$ 8	HNO_3 (conc.)	80–85	$\text{CCl}_2=\text{CClC}(\text{NO}_2)=\text{CCl}_2$ 9	40	25
$\text{Cl}_2\text{C}=\text{CClCH}=\text{CCl}_2$ 8	$\text{HNO}_3 - \text{H}_3\text{PO}_4$ (10 : 1)	—	$\text{CCl}_2=\text{CClC}(\text{NO}_2)=\text{CCl}_2$ 9	60	26
$\text{Cl}_2\text{C}=\text{CClCH}=\text{CCl}_2$ 8	$\text{HNO}_3 - \text{H}_2\text{SO}_4$ (10 : 1)	—	$\text{CCl}_2=\text{CClC}(\text{NO}_2)=\text{CCl}_2$ 9	55	26
$\text{CBrCl}=\text{CCH}=\text{CCl}_2$ Cl 14	HNO_3 (conc.)	80–85	$\text{CBrCl}=\text{CClC}(\text{NO}_2)=\text{CCl}_2$ 15	40	27
$\text{CBrCl}=\text{CCH}=\text{CCl}_2$ Cl 14	$\text{HNO}_3 - \text{H}_3\text{PO}_4$ (10 : 1)	95–100	$\text{CBrCl}=\text{CClC}(\text{NO}_2)=\text{CCl}_2$ 15	58	28
$\text{Br}-\text{C}(\text{Cl})=\text{CH}=\text{CCl}_2$ 17	HNO_3 (conc.)	80–85	$\text{Br}-\text{C}(\text{Cl})=\text{C}(\text{NO}_2)=\text{CCl}_2$ 19	40	29
$\text{Br}-\text{C}(\text{Cl})=\text{CH}=\text{CCl}_2$ 17	$\text{HNO}_3 - \text{H}_3\text{PO}_4$ (10 : 1)	90–95	$\text{Br}-\text{C}(\text{Cl})=\text{C}(\text{NO}_2)=\text{CCl}_2$ 19	48–50	29
$\text{Cl}-\text{C}(\text{Br})=\text{CH}=\text{CCl}_2$ 18	HNO_3 (conc.)	80–85	$\text{CBrCl}=\text{CCBr}=\text{CCl}_2$ NO_2 20	35	29
$\text{Cl}-\text{C}(\text{Br})=\text{CH}=\text{CCl}_2$ 18	$\text{HNO}_3 - \text{H}_3\text{PO}_4$ (10 : 1)	90–95	$\text{CBrCl}=\text{CCBr}=\text{CCl}_2$ NO_2 20	50	29
$\text{H}-\text{C}(\text{Cl})=\text{CCl}=\text{CCl}_2$ 21	HNO_3 (conc.)	70–75	$\text{CCl}_2=\text{CClCCl}=\text{CCl}$ NO_2 22	49	31
$\text{H}-\text{C}(\text{Cl})=\text{CCl}=\text{CCl}_2$ 21	$\text{HNO}_3 - \text{H}_3\text{PO}_4$ (10 : 1)	90–95	$\text{CCl}_2=\text{CClCCl}=\text{CCl}$ NO_2 22	56	31
$\text{CHCl}=\text{CHCH}=\text{CHCl}$ 25	HNO_3 (conc.)	70	$\text{CCl}=\text{CHCH}=\text{CCl}$ NO_2 26	7.7	33
$\text{CHCl}=\text{CHCH}=\text{CHCl}$ 25	AcONO_2 in AcOH	20–25	$\text{CH}=\text{CHCH}=\text{CCl}$ + NO_2 27 NO_2 + $\text{CCl}=\text{CHCH}=\text{CCl}$ NO_2 26 NO_2	9.1 1.4	33
$\text{CBrCl}=\text{CHCH}=\text{CCl}_2$ 29	HNO_3 (conc.)	80–85	$\text{CCl}=\text{CHC}(\text{NO}_2)=\text{CCl}_2$ 28	10	30
$\text{CBrCl}=\text{CHCH}=\text{CCl}_2$ 29	$\text{HNO}_3 - \text{H}_3\text{PO}_4$ (10 : 1)	90–95	$\text{CCl}=\text{CHC}(\text{NO}_2)=\text{CCl}_2$ 28	18	36

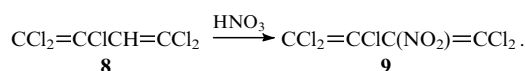
Recently, the nitration of butadiene by trifluoroacetyl nitrate has been proposed, the reagent being generated *in situ* from ammonium nitrate and trifluoroacetic anhydride. A mixture of 1,2- and 1,4-nitro-trifluoroacetates thus formed (**6** and **7**, respectively) was treated with potassium acetate in ether or by sodium hydride in THF to give one isomer of the nitrodiene **2** in 89% yield.^{23,24} On the basis of IR-spectrum, *E*-configuration was assigned to the diene **2**. The nitrotrifluoroacetoxylation of butadiene may be represented by the following scheme:



b. Synthesis of halogenonitrobutadienes

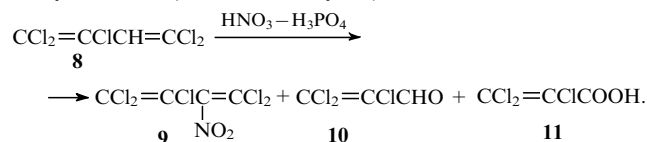
The direct nitration of the corresponding dienes is mostly used for the preparation of polyhalogenonitrobutadienes and products of their oxidative destruction.

The nitration of 1,1,2,4,4-pentachlorobutadiene (**8**) with concentrated HNO_3 occurs at the dichlorovinyl group by electrophilic substitution of the H atom by the nitro group with the formation of 2-nitropentachlorobuta-1,3-diene (**9**) in ~40% yield.²⁵

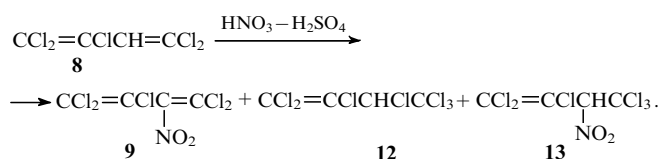


The same authors studied the interaction of the diene **8** with other nitration reagents.²⁶ It has been shown that the nitration of the diene **8** by a mixture of HNO_3 and H_3PO_4 (10:1) allowed one to increase the yield of the target product **9** up to 58%–60%, the duration of nitration was thus shortened three- to four-fold. Increase or decrease in the content of phosphoric acid in the reaction mixture increases the reaction time and decreases the yield of the nitrodiene.

The nitration of the diene **8** by nitric acid and the 10:1 HNO_3 – H_3PO_4 mixture is accompanied by oxidative destruction, which leads to trichloroacrolein **10** (in ~12% yield) and trichloroacrylic acid **11** (in ~5%–7% yield).

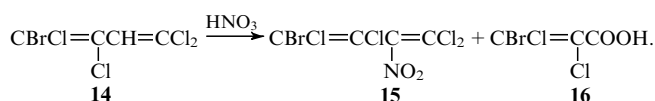


The nitrodiene **9** was synthesised in 54%–55% yield by nitration of the diene **8** by a mixture of HNO_3 and H_2SO_4 (10:1). The higher content of H_2SO_4 in the mixture results in the activation of side reactions of chlorination and nitrochlorination of the starting diene **8**, which lead to 1,1,2,3,4,4,4-heptachlorobut-1-ene (**12**) and 3-nitro-1,1,2,4,4,4-hexachlorobut-1-ene (**13**).



The nitration of mixed bromochlorobutadienes has been studied in detail using 1-bromo-1,2,4,4-tetrachlorobuta-1,3-diene (**14**) which contains a β,β -dichlorovinyl group, as an example. Its

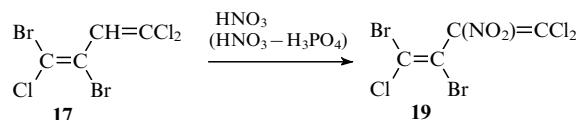
interaction with concentrated HNO_3 leads to 4-bromo-1,1,3,4-tetrachloro-2-nitrobuta-1,3-diene (**15**) (in 40% yield); bromodichloroacrylic acid (**16**) was found as a by-product.²⁷



If an $\text{HNO}_3(\text{conc.})$ – $\text{H}_3\text{PO}_4(\text{conc.})$ nitration mixture is used, the yield of the target product **15** is considerably increased, and under the optimum conditions amounts to 52%–53%.²⁸

The nitration of a mixture of two geometric isomers of bromochlorobutadiene **14** (*Z/E* = 25:75) resulted in the nitrodiene **15** in the form of two isomers in practically the same ratio. The individual isomers were isolated by column chromatography on silica gel.

The nitration of mixed pentahalogenobutadienes containing two Br atoms in the molecule have been studied using 1,2-dibromo-1,4,4-trichlorobuta-1,3-diene (**17**) and 1,3-dibromo-1,4,4-trichlorobuta-1,3-diene (**18**) as examples. Reaction of the *E*-isomer of the diene **17** with concentrated HNO_3 gave (*E*)-3,4-dibromo-2-nitro-1,1,4-trichlorobuta-1,3-diene (**19**) in 40% yield. If the mixture of concentrated HNO_3 and H_3PO_4 (10:1) was used for the nitration of the diene **17**, the yield of the nitrodiene **19** increased by 8%–10%.²⁹

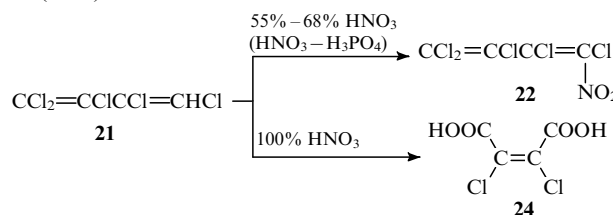


The dibromotrichlorodiene **18** behaves in nitration similarly to the diene **17**.²⁹ 1,3-Dibromo-2-nitro-1,4,4-trichlorobuta-1,3-diene (**20**) was obtained as one isomer (in 35% yield) by reaction of *E*-isomer of diene **18** with HNO_3 . The nitration of the diene **18** by the mixture of HNO_3 – H_3PO_4 (10:1) allowed one to increase the yield of the target product **20** to 48%–50%.

Thus, the nitration of all the above-discussed polyhalogenobutadienes containing the β,β -dichlorovinyl group† proceeds in the usual way with the substitution of the H atom by the nitro group.

The behaviour of halogenobutadienes containing α,β -dihalo-vinyl groups, in reaction with nitric acid has been studied only with the example of (*Z*)-1,1,2,3,4-pentachlorobuta-1,3-diene (**21**). The action of concentrated HNO_3 on the diene **21** results in the substitution of the only H atom by nitro group with the formation of 1,2,3,4,4-pentachloro-1-nitrobuta-1,3-diene (**22**) (in ~49% yield).³¹ The use of a nitration mixture consisting of concentrated HNO_3 and H_3PO_4 allows one to obtain the target nitrodiene **22** in 55%–56% yield.

Hexachlorobutadiene (**23**) (~6%), trichloroacrylic acid (**11**) (~8%), and dichloromaleic acid (**24**) (in ~4% yield) are the by-products of the reaction. The use of fuming HNO_3 directs the reaction towards the preponderant formation of the valuable acid **24** (60%).³²



† It is interesting to note that 1,1,4,4-tetrachlorobuta-1,3-diene with two β,β -dichlorovinyl groups under the action of 58%–60% HNO_3 gives the addition product — 1,1,4,4-tetrachloro-1,4-dinitrobut-2-ene. No products of the substitution of H atoms by the nitro group were registered.³⁰

$$\begin{array}{c}
 \text{O} \\
 \parallel \\
 \text{H}-\text{C}=\text{C}-\text{H} \\
 \parallel \\
 \text{O}
 \end{array}
 \xrightarrow{2\text{MeNO}_2}
 \begin{array}{c}
 \text{OH} \quad \text{OH} \\
 | \quad | \\
 \text{CH}_2-\text{CH}-\text{CH}-\text{CH}_2 \\
 | \qquad | \\
 \text{NO}_2 \quad \text{NO}_2
 \end{array}
 \xrightarrow{\text{AcOH}}
 \begin{array}{c}
 \text{AcO} \quad \text{OAc} \\
 | \quad | \\
 \text{CH}_2-\text{CH}-\text{CH}-\text{CH}_2 \\
 | \qquad | \\
 \text{NO}_2 \quad \text{NO}_2
 \end{array}
 \xrightarrow[\text{-AcOH}]{\text{KHCO}_3}
 \begin{array}{c}
 \text{CH}=\text{CHCH}=\text{CH} \\
 | \qquad | \\
 \text{NO}_2 \quad \text{NO}_2
 \end{array}$$

The diene **41** was synthesised by bromination of the diene **36** followed by dehydrobromination of 1,2,3,4-tetrabromo-1,4-di-

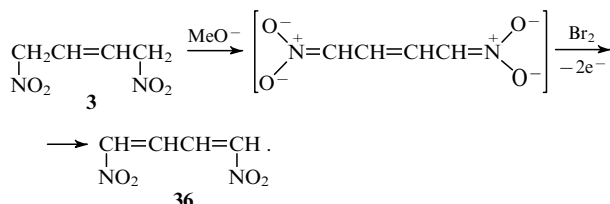
$$\begin{array}{c}
 \text{CH}=\text{CHCH}=\text{CH} \xrightarrow{2\text{Hal}_2} \text{CHHalCHHalCHHalCHHal} \xrightarrow{-2\text{HHal}} \\
 \text{NO}_2 \qquad \qquad \qquad \text{NO}_2 \qquad \qquad \qquad \text{NO}_2 \qquad \qquad \qquad \text{NO}_2 \\
 \text{36} \qquad \qquad \qquad \qquad \qquad \qquad \text{40, 42} \\
 \longrightarrow \text{CHal}=\text{CHCH}=\text{CHal} \\
 \text{NO}_2 \qquad \qquad \qquad \text{NO}_2 \\
 \text{26, 41}
 \end{array}$$

The conditions of the elimination reactions and the yields of the nitrodienes thus obtained are given in Table 2.

Starting compound	Eliminating reagent	Nitrobutadiene	Yield (%)	Ref.
$\text{NO}_2\text{CH}_2\text{CH}=\text{CHCH}_2\text{NO}_2$ 3	Na ₂ CO ₃	$\text{CH}_2=\text{CHCH}=\text{CHNO}_2$ 2	—	21
$\text{NO}_2\text{CH}_2\text{CH}=\text{CHCH}_2\text{ONO}_2 + \text{NO}_2\text{CH}_2\text{CHCH}=\text{CH}_2$ 4 5	Et ₃ N	$\text{CH}_2=\text{CHCH}=\text{CHNO}_2$ 2	—	22
$\text{ICH}_2\text{CH}=\text{CHCH}_2\text{NO}_2$ 31	Pb(OAc) ₄	$\text{CH}_2=\text{CHCH}=\text{CHNO}_2$ 2	35	38
$\text{CH}_2=\text{CHCHCH}_2\text{OAc}$ NO_2	K ₂ CO ₃	$\text{CH}_2=\text{CHC}=\text{CH}_2$ NO_2 32	50	39
$\text{CH}_2=\text{CHCCH}_2\text{OH}$ NOONa	HCl	$\text{CH}_2=\text{CHC}=\text{CH}_2$ NO_2 32	—	40
$\text{NO}_2\text{CH}_2\text{CH}(\text{Cl})\text{CH}(\text{Cl})\text{CH}_2\text{NO}_2$ 37	Pb(OAc) ₄	$\text{NO}_2\text{CH}=\text{CHCH}=\text{CHNO}_2$ 36	40	41
$\text{NO}_2\text{CH}_2\text{CH}(\text{OAc})\text{CH}(\text{OAc})\text{CH}_2\text{NO}_2$ 39	KHCO ₃	$\text{NO}_2\text{CH}=\text{CHCH}=\text{CHNO}_2$ 36	85	42, 44
CHClCHClCHClCHCl NO_2 NO_2 40	Suspension of florisol	$\text{CCl}=\text{CHCH}=\text{CCl}$ NO_2 NO_2 26	99	44
CHBrCHBrCHBrCHBr NO_2 NO_2 42	2,6-Lutidine or 2-picoline	$\text{CBr}=\text{CHCH}=\text{CBr}$ NO_2 NO_2 41	85	45, 46
$(\text{NO}_2)_2\text{CH}-\text{CH}(\text{OAc})-\text{CH}(\text{OAc})-\text{CH}(\text{NO}_2)_2$ 44	Alkalies, NaOMe, aniline	$(\text{NO}_2)_2\text{CH}=\text{CHCH}=\text{CH}(\text{NO}_2)_2$ 43	—	51

3. Other methods for the synthesis of nitrobutadienes

Among other methods for the synthesis of the nitro derivatives of butadiene, one should mention first of all the oxidation of the salts of 1,4-dinitrobut-2-ene into 1,4-dinitrobuta-1,3-diene **36**.^{52–54} The addition of 1 mol of an oxidising agent (Br_2 , I_2 , $\text{K}_3\text{Fe}(\text{CN})_6$, AgNO_3) to the suspension of **3** in ether gives dinitrobutadiene **36** in 50%–55% yield. Bromine, which has high oxidising potential, is the most universal oxidising agent.⁵³

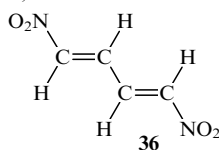


The treatment of the butene **3** with methanolic KOH and bromine in methanol at -10°C gives diene **36** in 79% yield.⁴⁵

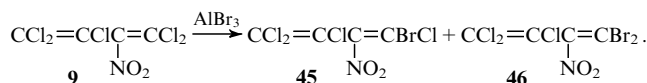
The redox titration has demonstrated that the transformations of the conjugated dianions proceeded as two-electron redox processes.⁵⁵

It has been found⁵⁵ that the nitrodiene **36** can be prepared in 50% yield by reaction of butene **3** with butyllithium in a mixture of THF and hexametaphol at -70 to -50°C and subsequent bromination at this temperature. The nitrodiene **2** was also found in the reaction products in 5% yield. The compound **36** presumably resulted from the two-electron oxidation process.

On the basis of a combination of several spectral data^{46, 54, 57} the *E,E*-structure was ascribed to the diene **36**.

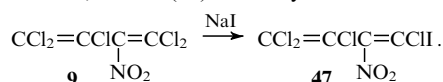


A series of mixed nitroperhalogenobutadienes was obtained by exchange of the halogen atoms. Thus in the reaction of the nitrodiene **9** with AlBr_3 substitution of one or two Cl atoms by Br in the nitrodichlorovinyl fragment occurs depending on the ratio of the reagents.⁵⁸ At the ratio of **9**: AlBr_3 = 1:1 in refluxing bromoethane, a mixture of mono- and di-substituted products, 1-bromo-1,3,4,4-tetrachloro-2-nitrobuta-1,3-diene (**45**) and 1,1-dibromo-3,4,4-trichloro-2-nitrobuta-1,3-diene (**46**) in the molar ratio of 1.0:5.3 (GLC) is formed in 71% total yield.

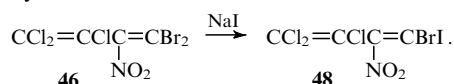


The use of an excess of AlBr_3 (**9**: AlBr_3 = 1.0:1.5) gives the diene **46** in 55% yield. The nitrobutadiene **46** was also prepared in 71% yield by the action of AlBr_3 on the diene **45**.

The reaction of the nitrodiene **9** with sodium iodide in acetone (the Finkelstein reaction) results in 1,3,4,4-tetrachloro-1-iodo-2-nitrobuta-1,3-diene (**47**) in 59% yield.⁵⁸

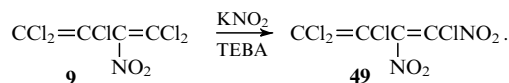


The butadiene **46** also exchanges only one Br atom for I in the nitrodibromovinyl fragment under analogous conditions, giving 1-bromo-3,4,4-trichloro-1-iodo-2-nitrobuta-1,3-diene (**48**) in 54% yield.⁵⁸



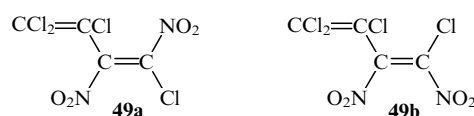
The substitution of halogen atoms by nitrite ion, which has been well studied in the alkyl halide series, is represented by only two examples in the synthesis of nitrobutadienes.

1,3,4,4-Tetrachloro-1,2-dinitrobutadiene (**49**) was synthesised by the reaction of 2-nitrodiene **9** with potassium nitrite in aqueous medium with triethylbenzyl ammonium chloride (TEBA) as a phase-transfer catalyst.⁵⁹

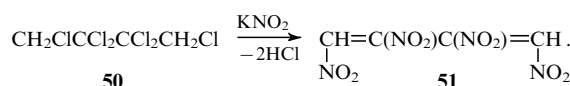


The study of the effect of temperature, the duration of reaction, the reagent ratio, and the KNO_2 concentration on the course of the reaction has shown that the optimum conditions are as follows: 5% TEBA and a twofold molar excess of the 30% KNO_2 solution. In all cases, the conversion of the nitrodiene **9** was not complete, the yield of **49** did not exceed 29% with respect to the diene **9** consumed. The use of other phase-transfer catalysts, *e.g.*, tetraethylammonium chloride, dibenzo-18-crown-6, and 18-crown-6 gave no advantages in comparison with TEBA.

The nitrobutadiene **49** was obtained as a 3:1 mixture of two isomers, which were separated by column chromatography on silica gel and characterised by spectroscopy. It was estimated that the main product was the *Z*-isomer **49a**, the other compound the *E*-isomer **49b**:



1,2,3,4-Tetranitrobuta-1,3-diene (**51**) was obtained by the reaction of 1,2,2,3,3,4-hexachlorobutane (**50**) with KNO_2 in methoxyethanol at 120°C and isolated as salt in 91% yield.⁶⁰

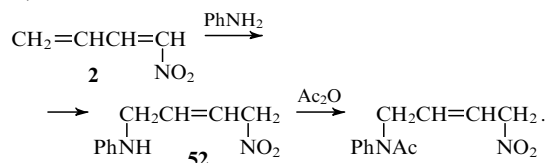


III. Addition reactions

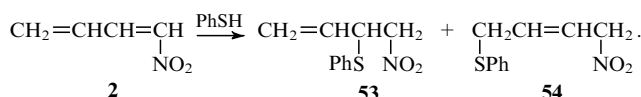
The development of methods for the synthesis of nitro- and nitrohalogen derivatives of butadiene paralleled their examination as the starting compounds for numerous chemical reactions.

1. Nucleophilic reactions

As a result of the electron-accepting effect of the nitro group, nitrobutadienes are able to participate in nucleophilic addition reactions. It has been shown, for example, that the simplest nitroalkadiene, 1-nitrobutadiene **2**, readily reacts with various nucleophilic reagents. The direction of these reactions depends on the nature of the nucleophile. They may occur both at the 1,2- and 1,4-positions of the diene system. Thus, the reaction of the nitrodiene **2** with aniline gives mostly 1-anilino-4-nitrobut-2-ene **52** (57%) characterised as the *N*-acetate.²⁴

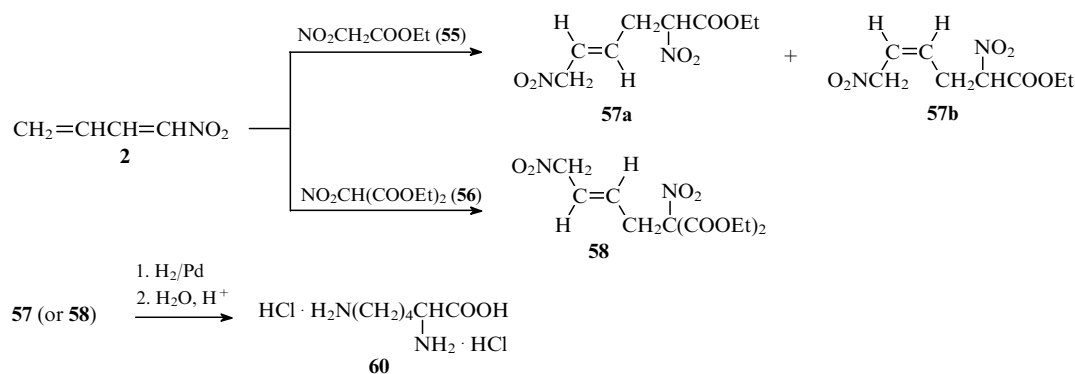


The reaction of the nitrodiene **2** with ethanethiol preferentially occurs at the nitrovinyl group.⁶¹ The diene **2** reacts analogously with thiophenol to give the 1,2-adduct **53** in 54% and the 1,4-adduct in 13% yield:²⁴



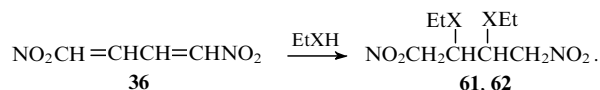
The addition of C-nucleophiles to nitrodienes has been studied using the reaction of the compound **2** with ethyl nitroacetate **55**

Scheme 2



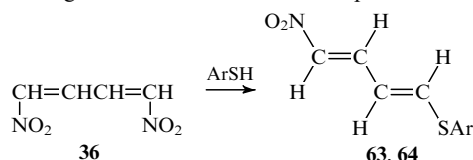
and nitromalonate **56** in the presence of triethylamine as examples.^{22, 62, 63} This reaction occurs at the 1,4-position and results in ethyl 2,6-dinitrohex-4-enoate (**57**) and diethyl 1,5-dinitropent-3-ene-1,1-dicarboxylate (**58**) in 32% and 35% yields respectively. The ester **57** was obtained in the form of two isomers, (*E*)-**57a** and (*Z*)-**57b**; also in the second case the product of bis-addition, ethyl 1,5,9-trinitronona-2,7-diene-5-carboxylate (**59**) was isolated (Scheme 2). Hydrogenation of the adducts **57** and **58** on a palladium catalyst in acidic ethanol resulted in the formation of ethyl 2,6-diaminohexanoate, its hydrolysis gave D,L-lysine hydrochloride **60** in 70% yield. This reaction is an original route for the preparation of a valuable amino acid, lysine.

In reactions with nucleophiles, dinitrobutadienes may give addition products of one or two molecules of the reagent as well as substitution products. The addition product of two molecules of ethanol, 2,3-diethoxy-1,4-dinitrobutane (**61**), has been isolated in 52% yield in the treatment of the nitrodiene **36** with ethanol at 25 °C.⁶⁴ The product of bis-addition **62** is also formed in the reaction of the diene **36** with ethanethiol.



X = O (**61**), S (**62**).

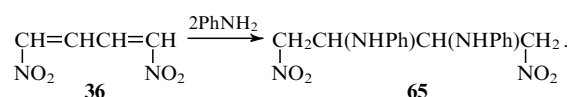
With more reactive arenethiols, the nitrodiene **36** gives the product of substitution of a nitro group, *e.g.* its reaction with thiophenol results in 4-nitro-1-phenylthiobuta-1,3-diene (**63**) in 42% yield.⁶⁵ The reaction of the nitrodiene **36** with *p*-toluenethiol in methanol proceeds analogously and gives 4-nitro-1-*p*-tolylthiobuta-1,3-diene (**64**) (28%).⁶⁶ In this case, presumably, the nucleophilic addition-elimination is realised. The direction of nucleophilic attack at the terminal C atom, which has never been observed earlier in reactions of aliphatic dinitrodiene with other nucleophiles, has been rationalised⁶⁶ as being due to the steric factors: the bulky reagent molecule and the stability of the conjugated system formed. On the basis of ^1H NMR spectra, an *E,E*-configuration was ascribed to compounds **63** and **64**.



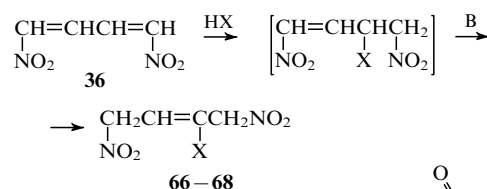
Ar = Ph (**63**); *p*-MeC₆H₄ (**64**).

The oxidation of the 1-arylthio-4-nitrobutadienes **63**, **64** was used for the preparation of hitherto unknown and inaccessible 4-nitro-1-sulfonylbutadienes.⁶⁷

In the reaction of the dinitrodiene **36** with aniline, the C(2) and C(3) atoms are subjected to nucleophilic attack to give the product of bis-addition, 2,3-dianilino-1,4-dinitrobutane (**65**) isolated as a mixture of D,L- and *meso*-isomers in 65% overall yield.⁶⁸



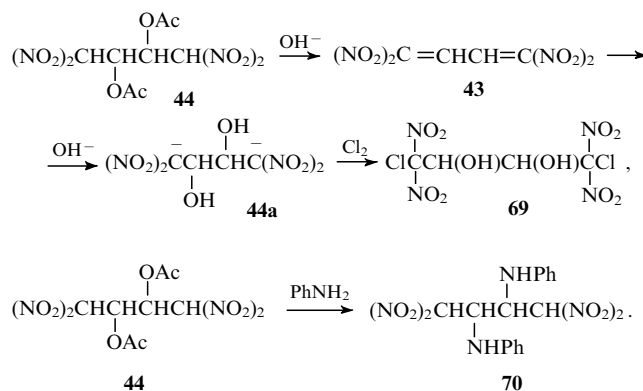
The nitrodiene **36** reacts with CH-acids to give the addition product at one of the nitrovinyl fragments; the other nitrovinyl fragment isomerises in the presence of a base into the nitroallyl system, which does not enter into addition reactions.^{47, 51}



X = $-\text{CH}(\text{COOH})_2$ (**66**), $-\text{CH}(\text{COOPh})_2$ (**67**), $-\text{CH}(\text{COOMe})_2$ (**68**);
B = base.

It has already been mentioned that tetranitrobutadiene **43** is unstable. However it was possible to accomplish some chemical transformations of this compound *in situ* without its isolation from the reaction mixture. Thus the reaction of 1,1,4,4-tetranitrobutane-2,3-diol diacetate (**44**) with an equivalent quantity of alkali in ether and subsequent chlorination of the formed tetranitrobutandiol salt **44a** results in 1,4-dichloro-1,1,4,4-tetranitrobutane-2,3-diol (**69**) (Scheme 3). The diacetate **44** is readily deacetoxyated even under the action of weak bases. Its treatment with aniline resulted in a quantitative yield of 2,3-dianilino-1,1,4,4-tetranitrobutane (**70**).⁵¹

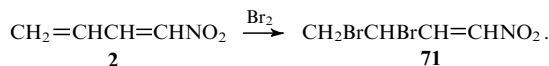
Scheme 3



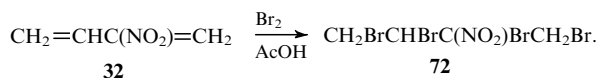
2. Electrophilic reactions

Nitrobutadienes are far less reactive in electrophilic substitution reactions in comparison with butadiene, as the nitro group imparts a pronounced electrophilic character to the diene system. Only the reactions of electrophilic halogenation of nitrobutadienes are known. It has been found²⁰ that the nitrobutadiene **2**

adds bromine at the vinyl group with the formation of the dibromide **71** (no yield is reported).



The bromination of the nitrobutadiene **32** in chloroform proceeds slowly, however in a more polar solvent, such as acetic acid, it quickly adds two Br₂ molecules to form the tetrabromide **72**.⁶⁹

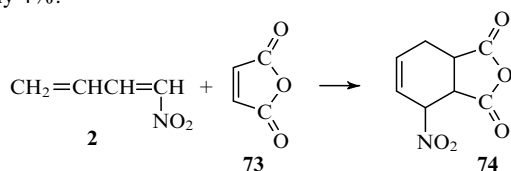


The bromination of the dinitrodiene **36** proceeds analogously, its product, tetrabromodinitrobutane **42**, is used in the synthesis of dibromodinitrodiene **41**.^{44–50}

The chlorination of the nitrodiene **36**, which results in the formation of the tetrachlorodinitrobutane **40** has been discussed earlier⁴⁴ (see Section II.2).

3. Cycloaddition reactions

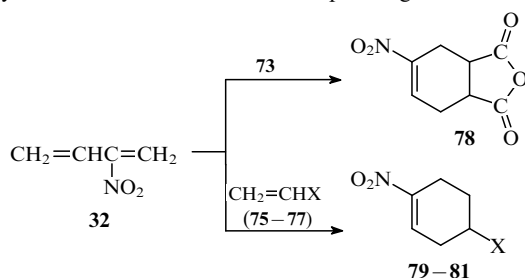
The Diels–Alder reaction involving nitrobutadienes has not been adequately explored. It is known²⁰ that the 1-nitrodiene **2** reacts with maleic anhydride **73**, however the yield of the adduct **74** is only 4%.



The nitrodiene **2** does not react with benzoquinone, α -naphthoquinone, acrylonitrile, acrolein, and dimethyl acetylenedicarboxylate even at 90–100 °C, at > 100 °C the reaction mixture resinifies.²⁰

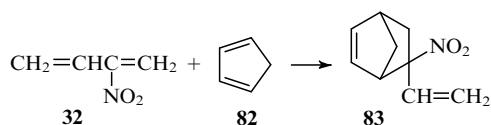
The 2-nitrodiene **32** has been shown to dimerise spontaneously in the process of its synthesis.⁷⁰ Dimerisation occurs as a [4 + 2]-cycloaddition reaction in which one nitrodiene molecule acts as a diene and the second one is a dienophile.

The nitrodiene **32** acts as a diene component in reactions with the maleic anhydride **73**, nitroethylene **75**, acrolein **76**, and acrylonitrile **77** and forms the corresponding adducts **78–81**.⁶⁹



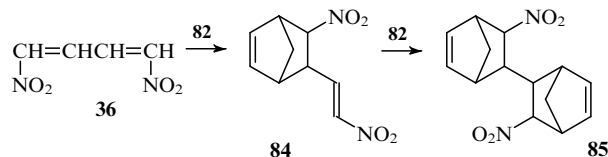
X = NO₂ (**75**, **79**), CHO (**76**, **80**), CN (**77**, **81**).

The nitrovinyl fragment in the molecules of 2-nitrodienes manifests dienophile properties. Thus the reaction of the nitrodiene **32** with cyclopentadiene **82** gives the adduct **83**.⁶⁹



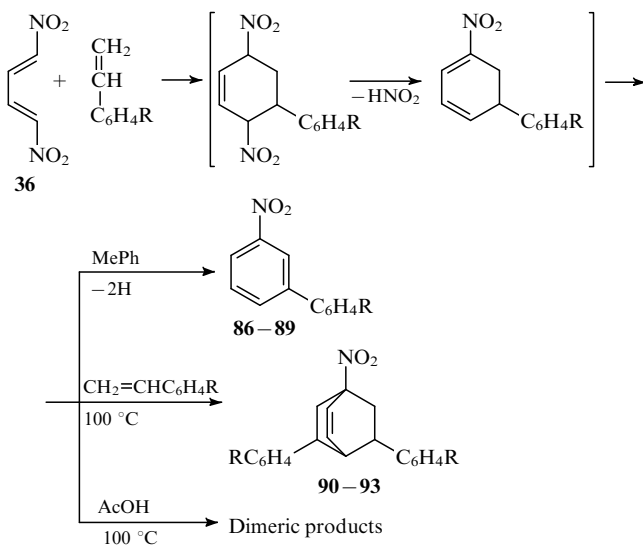
The behaviour of the diene **36** with pronounced electrophilic properties in the Diels–Alder reaction has been studied most extensively. Compound **36** has been shown to participate in reactions both as a diene and as a dienophile.^{47, 70–72} It acts as a

dienophile in the reaction with cyclopentadiene **82**. Thus at room temperature (48 h) 1 mol of diene **82** is added to the 1,2 position of the nitrodiene **36** to give 2-nitro-3-(2-nitroethenyl)bicyclo[2.2.1]hept-5-ene (**84**) in a 57% yield. If compound **84** is refluxed with the diene **82** in benzene for 8 h, the addition of the second mole of diene at the exocyclic double bond occurs with the formation of 3,3'-dinitro-2,2'-bis(bicyclo[2.2.1]hept-5-enyl) (**85**) (in 60% yield).



The nitrodiene **36** does not react with the anhydride **73**, which is a typical dienophile, *i.e.* it is inactive in the classical Diels–Alder synthesis. It turned out, however, that **36** undergoes the reverse Diels–Alder synthesis with nucleophilic dienophiles. It acts as a diene-acceptor in reactions with styrene and its derivatives, and the second components act as dienophiles-donors. The reaction of nitrodiene **36** with equimolar quantities of styrene and its *p*-substituted derivatives results in 1,4-adducts (Scheme 4), which spontaneously eliminate HNO₂ and are converted, depending on the reaction conditions, into either the corresponding 3-nitrobiphenyls **86–89** (on refluxing in toluene), or the bicyclic nitrocompounds **90–93** (on heating with the excess of styrene), or dimers (on heating with acetic acid).^{70–72}

Scheme 4



R = H (**86**, **90**), *p*-Cl (**87**, **91**), *p*-Br (**88**, **92**), *p*-Me (**89**, **93**).

IV. Substitution reactions

It is known that the occurrence of nucleophilic substitution reactions in the series of chlorine derivatives of butadiene depends to a considerable extent on the number of Cl atoms in the molecule and the nature of the terminal group and sometimes requires drastic conditions.⁷³

The development of convenient methods for the synthesis of highly electrophilic halogenonitrobutadienes allowed one to study in detail their behaviour in nucleophilic vinyl substitution reactions. The necessity of the studies of these reactions has been proved by quantum-chemical calculations that have been performed for a few halogen-substituted nitrobutadienes.

1. Quantum-chemical calculations

The quantum-chemical calculations of spatial and electronic structures were performed by semi-empirical methods CNDO/2,

Table 3. Effective charges (q) on atoms in halogenonitrobutadiene molecules (quantum-chemical calculation).

Compound	Method of calculation	q						
		C(1)	C(2)	C(3)	C(4)	N _i	N _t	O
9	CNDO/2	+0.118	+0.066	+0.112	+0.085	+0.453	—	−0.293
9	MINDO/3	+0.471	−0.272	+0.111	+0.343	+1.120	—	−0.550
9	MNDO	+0.127	−0.029	−0.008	+0.104	+0.188	—	−0.070
<i>E</i> - 15	MNDO	+0.134	−0.031	+0.005	+0.021	+0.362	—	−0.297
<i>Z</i> - 15	MNDO	+0.134	−0.028	+0.005	+0.022	+0.361	—	−0.298
<i>E</i> - 22	MNDO	+0.018	+0.083	−0.012	+0.078	—	+0.480	−0.290
<i>Z</i> - 22	MNDO	+0.019	+0.085	−0.030	+0.079	—	+0.472	−0.293
<i>E</i> - 28	MNDO	+0.026	+0.025	−0.070	+0.138	+0.475	+0.469	−0.293
<i>Z</i> - 28	MNDO	+0.028	+0.017	−0.052	+0.119	+0.477	+0.468	−0.297

Note. N_i and N_t are internal and terminal N atoms respectively. The averaged charge values are given for O atoms.

MINDO/3, and MNDO^{74–76} for the nitrobutadienes **9**, **15**, **22**, and **28**. It has been shown using diene **9** as an example that the results obtained by these methods are in satisfactory agreement with each other.⁷⁵

The molecules of mononitrodienes **9**, **15**, and **22** were found to be nonplanar with vinyl groups located in the planes that are virtually mutually perpendicular and with a violated conjugation in the diene chain. The molecule of dinitrodiene **28** exists in a nonplanar *s-trans*-conformation with the torsion angle C=C–C=C of 142.8°. The main geometric parameters of the molecules, such as bond lengths and angles, are in agreement with the analogous values for related compounds.^{2,77}

The lowest unoccupied molecular orbital (LUMO) is mostly (67%–85%) localised at the dihalogenonitrovinyl fragment of the molecule, mostly at the C atom adjacent to the =C(NO₂)– group and with the maximum positive charge. Consequently, the position adjacent to =C(NO₂)– is the most favourable for nucleophilic attack in the dihalogenonitrovinyl group. However, the exceptionally high positive charge at the N atom of the nitro group makes possible also the attack of hard nucleophiles at the =C–NO₂ fragment (Table 3).

The highest occupied molecular orbital (HOMO) is mostly (~70%) localised at the trihalogenovinyl group. In comparison with highly electrophilic dihalogenonitrovinyl groups, which represent hard electrophilic centres, the trihalogenovinyl fragments are soft electrophilic centres. The monochloronitrovinyl group in the nitrodiene **28** is less electrophilic than the dichloronitrovinyl group.

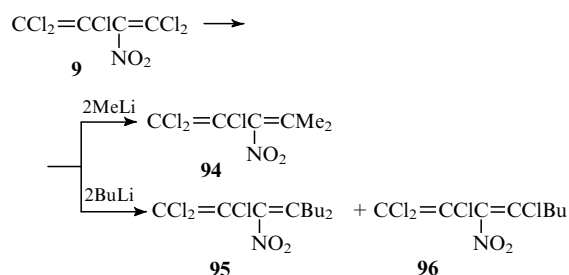
Thus, the quantum-chemical analysis shows that halogenonitrodienes must be active in processes of nucleophilic vinylic substitution ($S_N\text{Vin}$).

2. Interaction with C-nucleophiles

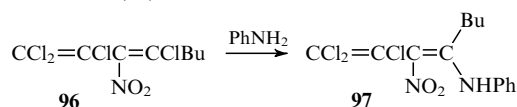
Reactions of halogenonitrobutadienes with organolithium compounds, which should be described as soft nucleophiles, according to the hard and soft acid-base principle have been studied only for mononitrodienes **9** and **22**.

The reaction of the nitrodiene **9** with methyl lithium (**9**: MeLi = 1:2, −75 to −70 °C) gives 1,1,2-trichloro-4-methyl-3-nitropenta-1,3-diene (**94**) (in 63% yield).^{78,79}

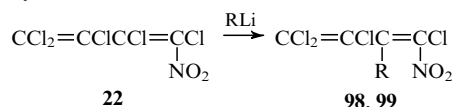
The reaction of the nitrodiene **9** with *n*-butyllithium under the same conditions results in a mixture of products of di- and monosubstitution, viz., 4-butyl-1,1,2-trichloro-3-nitroocta-1,3-diene (**95**) and 1,1,2,4-tetrachloro-3-nitroocta-1,3-diene (**96**), in the molar ratio of 1.5:1 in 58% overall yield. Increase in the amount of butyllithium practically does not change the ratio of the products formed, but decreases their overall yield. At the equimolar reagents ratio, the monosubstituted product **96** was isolated in 30% yield. It should be noted that the substitution is accompanied by considerable resinification.



The residual Cl atom of the nitrovinyl group of the monobutyl derivative **96** is readily substituted under the action of aniline, which results in the formation of 4-anilino-1,1,2-trichloro-3-nitroocta-1,3-diene (**97**).

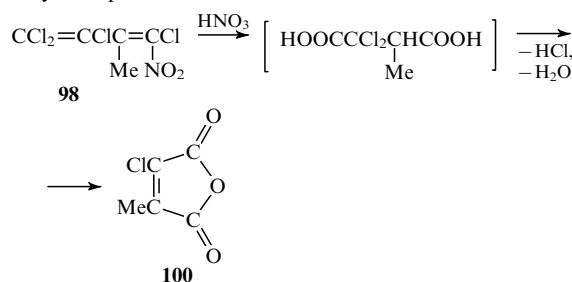


In contrast to the 2-nitrodiene **9**, the 1-nitrodiene **22** reacts with both methyl- and butyllithium with the substitution of only the Cl atom (at position 2) and the formation of the corresponding 2-alkyl-1,3,4,4-tetrachloro-1-nitrobuta-1,3-dienes (**98** and **99**).⁸⁰



R = Me (**98**), Bu (**99**).

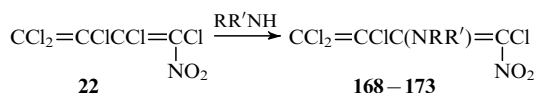
Under the optimum conditions (**22**: RLi = 1.0:1.2, −75 °C) the yield of the products is 36%–38%. The structure of the alkadienes **98** and **99** has been confirmed by spectral data and by a reaction of the butadiene **98** with fuming nitric acid leading to the formation of chlorocitraconic anhydride (**100**) and some other carbonyl compounds.



3. Interaction with thiols

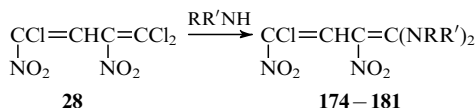
The reactions of halogenonitrobutadienes with thiols, which, according to the Pearson's scale, are soft nucleophiles, have mostly been studied using pentahalogenodienes with terminal and inter-

The interaction of 1-nitrodiene **22** with amines occurs with substitution of only the α -Cl atom in α,β -dichloro- β -nitrovinyl group to give 2-amino-1,3,4,4-tetrachloro-1-nitrobuta-1,3-dienes (**168**–**173**) in 57%–89% yields.^{31,93} X-Ray structural analysis has shown that **168**–**173** have *E*-configurations.⁹⁴



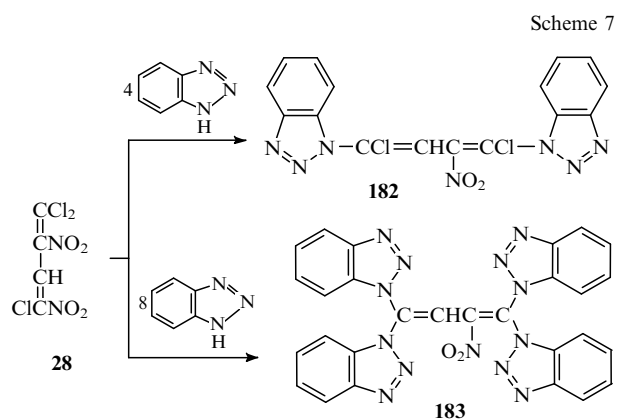
R = H; R' = Ph (**168**), *m*-MeC₆H₄ (**169**), CH₂Ph (**170**), Bu^t (**171**);
RR' = CH₂(CH₂)₃CH₂ (**172**), (CH₂)₂O(CH₂)₂ (**173**).

The reaction of the dinitrodiene **28**, the molecule of which has two types of chloronitrovinyl fragments, with primary and secondary amines leads to the substitution of two geminal Cl atoms in the β,β-dichloro-α-nitrovinyl group with the formation of the corresponding 4,4-diamino-1-chloro-1,3-dinitrobuta-1,3-dienes (**174–181**) in 55%–75% yields.⁹⁵



R = H; R' = Ph (**174**), CH₂Ph (**175**), *m*-MeC₆H₄ (**176**),
2,4-Me₂C₆H₃ (**177**), Bu^t (**179**);
R = R' = CH₂Ph (**178**);
R – R' = CH₂(CH₂)₃CH₂ (**180**), (CH₂)₂O(CH₂)₂ (**181**).

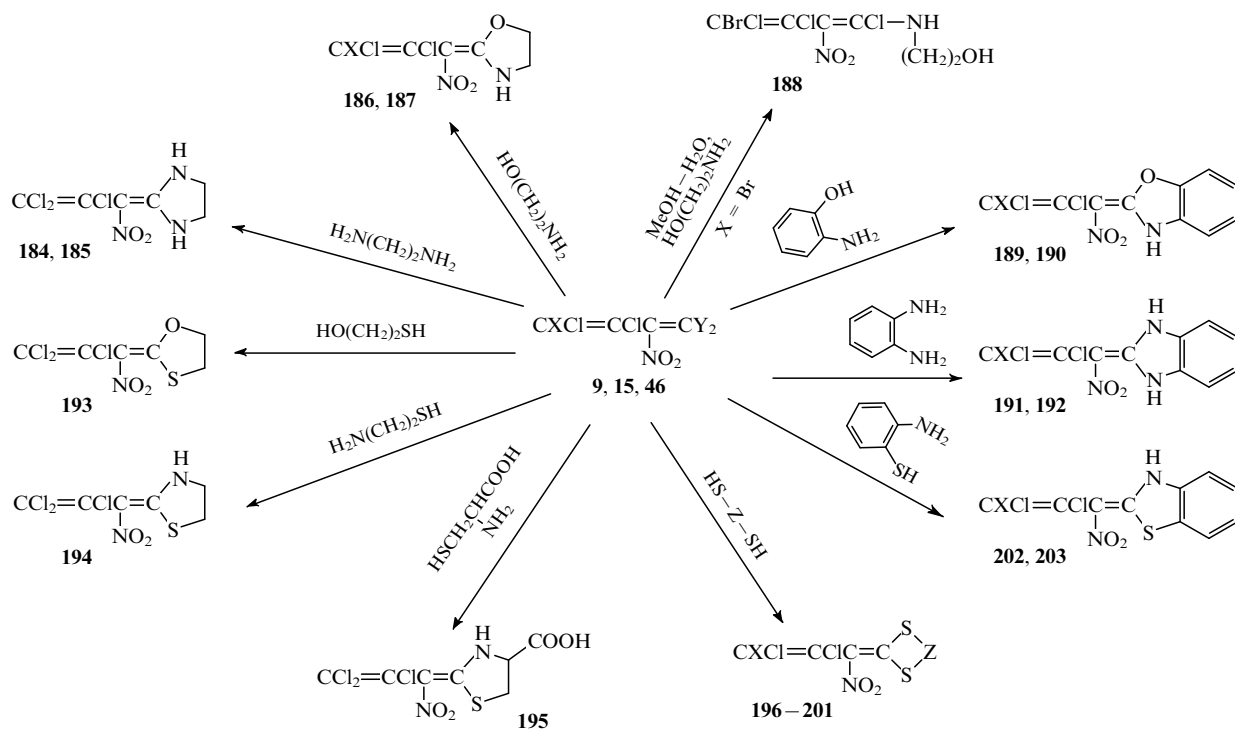
The reaction of the dinitrobutadiene **28** with benzotriazole occurs with participation of both nitrovinyl groups.^{36,91} When a 1 : 4 mixture of diene **28** and benzotriazole was refluxed in ether, the substitution of the NO₂ group in the chloronitrovinyl fragment and one of the geminal Cl atoms in dichloronitrovinyl group by the azole residues occur to form 1,4-di(1-benzotriazolyl)-1,4-dichloro-2-nitrobuta-1,3-diene (**182**) in 55% yield. With a larger excess of benzotriazole (eightfold), the substitution of all the remaining Cl atoms occurs to give 1,1,4,4-tetra(1-benzotriazolyl)-2-nitrobuta-1,3-diene (**183**) in 45% yield (Scheme 7).



6. Reactions with bifunctional nucleophilic reagents

Polyhalogenonitrobutadienes react readily with various bifunctional nucleophiles, which allows one to synthesise a series of heterocyclic systems. On the basis of nitrodiene **9**, **15**, and **46**, preparative methods for the synthesis of earlier inaccessible heterocyclic compounds, containing the trihalogeno-1-nitropropenylidene radical in the side chain have been developed.^{85,96–99} In particular, the imidazolidine derivatives **184**, **185** were prepared by reaction of nitrodiene **9**, **15**, and **46** with ethylenediamine (Scheme 8), and reactions of the nitrodiene with monoethanolamine lead to the oxazolidine derivatives **186**, **187**. The nature of the solvent is very important for the reaction of the nitrodiene **15** with monoethanolamine. It turned out that the main reaction product in aqueous ethanol (5% H₂O) is the linear product **188**, i.e. monoethanolamine behaves as an N-nucleophile, which may

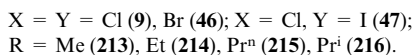
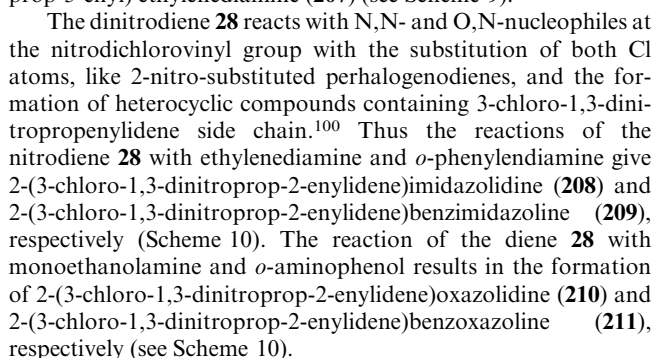
Scheme 8



9, **184**, **186**, **189**, **191**, **193–198**, **202**: X = Y = Cl;
15, **185**, **187**, **188**, **190**, **192**, **199–201**, **203**: X = Br, Y = Cl;
46, **184**, **186**, **189**, **191**, **193–198**, **202**: X = Cl, Y = Br.

Z = (CH₂)₂, (CH₂)₃, (CH₂)₆

The reaction of 1-nitrodiene **22** with bifunctional reagents occurs with the substitution of only one Cl atom in the α -position of the α,β -dichlorovinyl group to give the corresponding 2-mono-substituted products in preparative yields.³¹ The diene **22** reacts with monoethanolamine and cysteamine at the N-nucleophilic centre only in the presence of sodium ethoxide to form 1,3,4,4-tetrachloro-2-(2-hydroxyethylamino)-1-nitrobuta-1,3-diene (**204**) and 1,3,4,4-tetrachloro-2-(2-mercaptopethylamino)-1-nitrobuta-1,3-diene (**205**), respectively (Scheme 9).

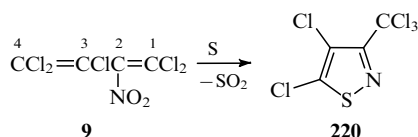


1-Ethoxypentachlorobutadiene **218** is known¹⁰⁴ to be useful in the synthesis of a valuable squaric acid.

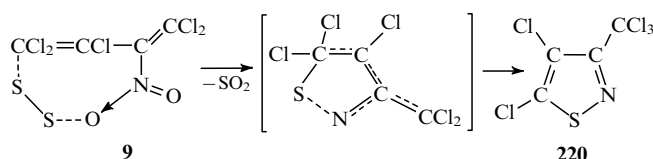
V. Other reactions

1. Synthesis of isothiazole derivatives

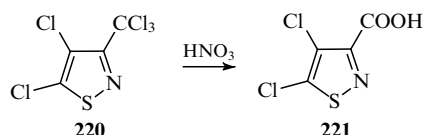
It is known that pentachlorobuta-1,3-dienes react with sulfur to form tetrachlorothiophenes.¹⁰⁵ Introduction of the nitro group into the polychlorodiene system considerably changes its reactivity. It has been recently shown^{106–108} that the reaction of the 2-nitrodiene **9** with sulfur occurs in a different direction with the participation of the nitro group and results in the formation of 4,5-dichloro-3-trichloromethylisothiazole (**220**) in 52% yield. This new, previously unknown reaction opens a convenient way to the construction of the isothiazole ring.



The unusual course of this reaction can be explained by the peculiarities of the electronic and molecular structure of the nitrodiene **9**. As has been shown by the quantum-chemical calculations,⁷⁵ C(4) and N atoms are closer to each other than C(4) and C(1) atoms, and the HOMO is mostly (about 70%) localised at the trichlorovinyl group, dominantly at the C(4) atom. Under the reaction conditions (180–200 °C), the sulfur molecules exist in the form of biradicals 'S_n·', the direction of their attack is determined by the HOMO structure. Thus a possible scheme for the process may be presented as the attack of a sulfur atom at C(4), subsequent elimination of SO₂ and cyclisation accompanied by migration of Cl atom.

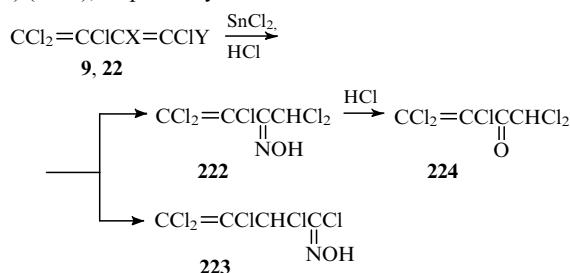


New methods for the preparation of previously inaccessible, valuable products, such as isothiazole derivatives have been developed. Thus starting from compound **220** a biologically important 4,5-dichlorothiazole-3-carboxylic acid (**221**) was obtained in 92% yield.^{107, 109}



2. Reduction of nitro-substituted pentachlorobuta-1,3-dienes

The reduction of 2-nitro- (**9**) and 1-nitropentachlorodienes (**22**) by tin dichloride in acidic medium proceeds in an unusual way and results in the formation of oximes of 1,1,3,4,4-pentachlorobut-3-en-2-one (**222**) (75%) and of 1,2,3,4,4-pentachlorobut-3-en-1-ol (**223**) (59%), respectively.¹¹⁰

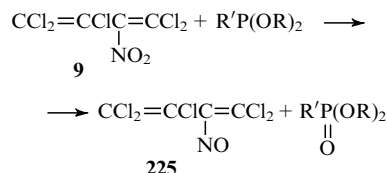


9: X = NO₂, Y = Cl;
22: X = Cl, Y = NO₂.

It has been found by spectral methods that oximes **222** and **223** are formed in one isomeric form: their configuration has been

determined by measuring the Nuclear Overhauser Effect (NOE) according to the NOEDIFF technique. The OH and CHCl₂ groups in the molecule of the oxime **222** are in the *syn*-position relative to the C=N bond, while in the oxime **223** the groups OH and CHClCCl=CCl₂ are in *anti*-position. It is interesting to note that the compound **222** hydrolyses on prolonged refluxing with concentrated HCl to form 1,1,3,4,4-pentachlorobut-3-en-2-one (**224**), which is used in the synthesis of medicinals.¹¹¹

Partial reduction of the nitrodiene **9** has been observed on its interaction with acyclic phosphites, 2-nitrosopentachlorobutadiene **225** (~ 10%) being one of the products.¹¹²



R = Me, CH₂CF₂CHF₂, CH(CF₃)₂; R' = NCO, RO.

* * *

Thus, nitrobutadienes and their halogen derivatives are valuable intermediates that may be used for the synthesis of compounds of different classes; original synthetic procedures were developed on their basis.

Of numerous methods of preparation of nitrobutadienes, the most convenient are the reactions of nitration of the corresponding dienes; they are especially promising in the synthesis of chlorosubstituted nitrobutadienes and their mixed bromochloro-containing analogues. The main types of chemical transformations of nitrobutadienes are addition and substitution reactions. The former are characteristic of the unsubstituted nitrodiene, while the latter are typical of their halogen derivatives.

Using halogenonitrobutadienes as examples, the formerly unknown peculiarities of the chemical behaviour of the nitro group in a polychlorodiene system have been elucidated. The possibility for the adequate interpretation of the regioselectivity of the nucleophilic vinylic substitution of the halogen atom and nitro group has been discussed in terms of the hard and soft acid-base principles.

It should, however, be noted that there are no data on fluorosubstituted nitrobutadienes. The development of the methods of their preparation and participation in chemical transformations is, to our mind, very interesting in both theoretical and practical aspects.

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^a — *Russ. Chem. Bull. (Engl. Transl.)*

^b — *Russ. J. Org. Chem. (Engl. Transl.)*

^c — *Chem. Heterocycl. Compd. (Engl. Transl.)*

^d — *Russ. J. Gen. Chem. (Engl. Transl.)*

^e — *Dokl. Chem. Technol., Dokl. Chem. (Engl. Transl.)*

^f — *J. Struct. Chem. (Engl. Transl.)*

Chemistry of inorganic sulfonates and sulfates of polyvalent iodine

T M Kasumov, A S Koz'min, N S Zefirov

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Abstract. Published data on the structure, properties and methods for the synthesis of inorganic sulfonates of polyvalent iodine are surveyed. Primary attention is devoted to the reactions of these compounds with organic substrates. The bibliography includes 129 references.

I. Introduction

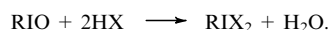
Derivatives of hypervalent iodine were described for the first time back in the late XIX century.¹ The unusual ability of iodine to exhibit valences of III and V in organic compounds immediately attracted the attention of chemists. The first monograph on the chemistry of polyvalent iodine containing a systematic account of the data on the synthesis of organic derivatives of iodine(III) and iodine(V) was published as early as 1914.² However, by the late 70s, the interest in compounds containing polyvalent iodine had markedly decreased. The data accumulated by that time have been surveyed fairly completely in two reviews.^{3,4}

In the early 80s, derivatives of polyvalent iodine again attracted the attention of researchers; this was due to the wide use of these compounds in various fields of organic synthesis.^{5–15}

The progress in the chemistry of polyvalent iodine derivatives is largely determined by the stability of these compounds. In particular, it is known that the high instability of aliphatic iodoso-derivatives is due to the extremely high nucleofugal properties of the iodoso-fragment, which is among the best known leaving groups.¹⁶ The main factor influencing the stability of both organic and inorganic derivatives of polyvalent iodine is the presence of highly nucleofugal ligands or counter-ions in their molecules. The stabilising influence of nucleofugal counter-ions or ligands on compounds of polyvalent iodine is clearly illustrated by the fact that these compounds normally contain anions of strong acids, such as tetrafluoroborate (BF_4^-),^{17,18} perchlorate (ClO_4^-),¹⁷ nitrate (NO_3^-),¹⁹ tosylate (TsO^-),^{20,21} etc, as ligands. Compounds containing anions of sulfonic acids [tosylate, trifluoromethanesulfonate (triflate, TfO^-), or methanesulfonate (mesylate, MsO^-)] as well as sulfate or hydrogensulfate are readily available and most

convenient to work with. It is the sulfonate derivatives of polyvalent iodine that are used most often in synthetic organic chemistry.²² One of the most important applications of polyvalent iodine sulfonates is the synthesis of covalent tosylates, triflates, fluorosulfates and other compounds,^{23–26} which are difficult to obtain by other methods.

Organic sulfonate derivatives of trivalent iodine, like the other representatives of this class of compound, have been referred to collectively as 'iodoso-salts',⁴ which reflects the fact that these compounds have been derived from iodoso-compounds and from the corresponding acids (similarly to the interaction between acids and bases to give salts).



This analogy is made even closer by the fact that treatment of any arylidososulfonate with an alkali affords the initial iodoso-derivative.⁴

'Iodoso-salts' are usually stable and can be easily prepared; therefore, they have found wide application in organic synthesis.

In recent years, a wide range of organic derivatives of polyvalent iodine with various sulfonate ligands at the iodine atom have been obtained, for example, phenyliodonium sulfates,²⁷ hydroxy(mesyloxy)iodoarenes,²⁸ perfluoroalkyliodoso(hydroxy)-tosylates^{29–31} and μ -oxodiphenylbis(trifluoro-methanesulfonate-*O*)diiodine.^{23,32} Study of the reactivities of these compounds has shown that derivatives of iodosylperfluoroalkanes and -arenes containing nucleofugal sulfonate and sulfate groups as substituents at the iodine atoms are convenient reagents for the transformation of alkenes into vicinal disulfonates and cyclic sulfates.^{27,28} At the same time, iodonium sulfates react with alkyl iodides as oxidative deiodinating agents. These reactions afford covalent monosulfates.³³

The properties of other organic sulfonate derivatives have been studied in detail by American^{21,34–38} and Japanese^{39–41} researchers. The chemical properties of these compounds have been surveyed in several reviews (see, for example, Refs 7, 42, and 43). However, inorganic sulfates and sulfonates of hypervalent iodine have not been even mentioned in these reviews. This stimulated us to consider systematically studies devoted to the structure, methods for the synthesis and the chemical properties of inorganic sulfonates and sulfates of polyvalent iodine. For convenience, in the subsequent discussion, the word 'inorganic' is omitted from the expression 'inorganic sulfonates and sulfates of polyvalent iodine'.

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II. The structure of sulfonates and sulfates of polyvalent iodine

Although the chemistry of organic derivatives of polyvalent iodine has been thoroughly studied and their nomenclature has been developed, there is still no exhaustive classification for the numerous sulfonates and sulfates of iodine (both organic and inorganic). One of the most widely used classifications of organic (including sulfonate and sulfate) derivatives of trivalent iodine is based on the formal account of the number of carbon and heteroatomic ligands at the iodine atom.^{4,7} According to this approach, related organic sulfonates are often considered as different structural classes. At the same time, the fact that all organic sulfonates and sulfates of polyvalent iodine [for example, $\text{RI}(\text{HSO}_4)_2$, $\text{R}_\text{F}\text{I}(\text{OSO}_2\text{F})_2$, $\text{PhI}^+\text{OSO}_3^-$, $\text{PhI}(\text{OH})\text{OTs}$, $\text{PhI}(\text{O}-\text{H})\text{OMs}$, $\text{Ar}_2\text{I}^+\text{OSO}_2\text{X}^-$ ($\text{X} = \text{OH}$, F , CF_3) and $\text{RPhI}^+\text{TfO}^-$] contain trivalent iodine is an argument for using a classification based on the valence state of iodine.

Classification of inorganic sulfonates and sulfates of polyvalent iodine takes into account the valence of the iodine atom and the types of sulfonate and sulfate ligands. The main types of known sulfonates and sulfates of polyvalent iodine are presented in Table 1. Inorganic derivatives are divided into two subgroups corresponding to I(III) and I(V).

Until the structure of iodine fluorosulfate as a derivative of I(III), $\text{I}(\text{OSO}_2\text{F})\text{I}$ (**1**), had been established unambiguously by X-ray diffraction analysis,⁴⁴ the majority of researchers^{45–49} had regarded this compound as a derivative of monovalent iodine. Despite the fact that no structural data have been obtained for iodine triflate, it would be legitimate to suggest (by analogy with the compound **1**) that this derivative, which is usually described by the formula $\text{I}(\text{SO}_2\text{CF}_3)_2$, also has a 'dimeric' structure, $\text{I}(\text{SO}_2\text{CF}_3)_2\text{I}$ (**2**). A convincing argument supporting this hypothesis is that these two reagents behave similarly in reactions with halogens.⁵⁰ Therefore, in the subsequent discussion, we use the formulae **1** and **2** rather than $\text{I}(\text{OSO}_2\text{F})$ and $\text{I}(\text{SO}_2\text{CF}_3)$ for iodine fluorosulfate and triflate, respectively.

Analysis of the published data indicates that the nomenclature of iodine sulfonates and sulfates is also ambiguous, since for these

compounds, various names are used. Table 1 presents the names that are used most frequently.

The structure of sulfonates and sulfates of polyvalent iodine has been studied using some representatives of this class as examples. In most cases, these compounds have been characterised by spectroscopic methods (^{19}F NMR, Raman, UV and IR spectroscopy), and the structure of iodine fluorosulfate **1** has been studied by X-ray diffraction analysis.⁴⁴ The most important feature of this structure is that both fluorosulfate groups are bound to one iodine atom (*i.e.* the formal oxidation state of one of the iodine atoms is +3, while that of the other atom is –1). With allowance for the two lone electron pairs present at the I(+3) atom, the geometry of its environment is a distorted trigonal bipyramid (a T-shaped structure), which is in line with the hypervalent nature of this compound. The lengths of the I–O bonds (2.26 Å) are greater than the sum of the covalent radii of I and O atoms indicating that these bonds are ionic to a certain extent. A significant feature of the geometry of the fluorosulfate **1** is the existence of an intermolecular O...I bond with a length of 3.05 Å. This bond is arranged almost across the I–I bond; this results in a distortion of the plane in which other bonds between the ligands and the 'central' iodine atom lie. The main structural parameters of the molecule **1** are shown in Fig. 1.

According to the Martin's classification of polycordinated derivatives of Group A elements,⁵¹ the compounds under consideration belong to the 10-I-3 type of structures. This means that the central iodine atom is surrounded by three ligands, and its valence shell contains ten electrons (including two lone pairs). The equatorial positions are occupied by the second iodine atom and by the two lone electron pairs. Fluorosulfate groups are in the axial positions. From numerous X-ray diffraction studies,^{52–56} it is known that organic derivatives of trivalent iodine are built similarly. The structure of $\text{I}(\text{SO}_2\text{F})_2\text{I}$ also resembles those of transition metal complexes.

The structures of iodine tris(fluorosulfates) and triflates have been studied by conductometry, calorimetry and spectroscopy. It was found that they behave as electrolytes in solutions of the corresponding acids. The high specific electrical conductivities of

Table 1. Types of inorganic sulfonates and sulfates of polyvalent iodine.

Ligand	Derivative of I(III)	Name of the compound	Derivative of I(V)	Name of the compound
OSO_2F	$\text{I}(\text{OSO}_2\text{F})_2\text{I}$	Iodine fluorosulfate	$\text{I}(\text{OSO}_2\text{F})_5$	Iodine pentafluorosulfate
	$\text{I}_2\text{HalOSO}_2\text{F}$, $\text{IHal}_2\text{OSO}_2\text{F}$, $\text{IHal}^+\text{Hal}^-\text{OSO}_2\text{F}$, ($\text{Hal} = \text{Cl}$, Br , I)	Iodine inter-halogen fluoro-sulfates	$\text{IF}_n(\text{OSO}_2\text{F})_{5-n}$	
	$\text{I}(\text{OSO}_2\text{F})_3$	Iodine tris(fluorosulfate)		
	$\text{M}[\text{I}(\text{OSO}_2\text{F})_4]$ ($\text{M} = \text{Na}$, K), $[\text{I}(\text{SO}_3\text{F})_2]^+[\text{Sn}(\text{SO}_3\text{F})_6]^{2-}$	Complex salts		
	$(\text{OI})\text{OSO}_2\text{F}$	Iodosyl fluorosulfate	$(\text{O}_2\text{I})\text{OSO}_2\text{F}$	Iodyl fluorosulfate
OSO_2CF_3	$\text{I}(\text{OSO}_2\text{CF}_3)_2\text{I}$	Iodine triflates		
	$\text{IHal}_2\text{OSO}_2\text{CF}_3$ ($\text{Hal} = \text{Cl}$, Br , I)	Iodine interhalogen triflates		
	$\text{I}(\text{OSO}_2\text{CF}_3)_3$	Iodine tris(triflate)		
	$\text{M}[\text{I}(\text{OSO}_2\text{CF}_3)_4]$ ($\text{M} = \text{K}$, Rb , Cs)	Complex salts		
	$(\text{OI})\text{OSO}_2\text{CF}_3$	Iodosyl triflate	$(\text{O}_2\text{I})\text{OSO}_2\text{CF}_3$	Iodyl triflate
SO_4	$\text{I}_2(\text{SO}_4)_3$	Iodine sulfate		
	$(\text{OI})_2\text{SO}_4$	Iodosyl sulfate		
HSO_4	$\text{I}(\text{HSO}_4)_3$	Iodine hydrogensulfate		
	$(\text{OI})\text{HSO}_4$	Iodosyl hydrogensulfate	$(\text{O}_2\text{I})\text{HSO}_4$	Iodyl hydrogensulfate
HS_2O_7			$(\text{O}_2\text{I})\text{HS}_2\text{O}_7$	Iodyl hydrogenpyrosulfate

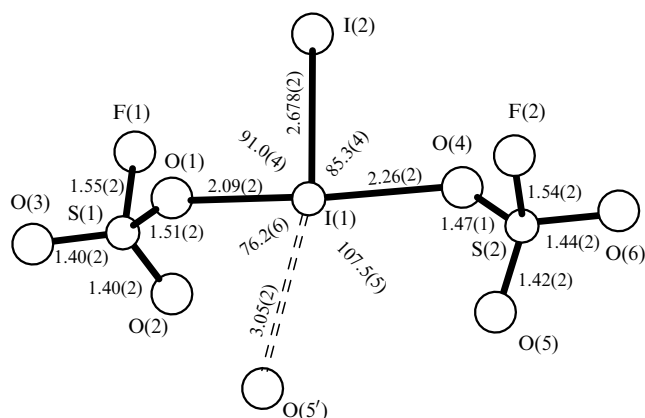


Figure 1. Molecular structure of $\text{I}(\text{OSO}_2\text{F})\text{I}$ (**1**). Bond lengths (Å) and bond angles (degrees) are presented.

iodine tris(sulfonates) have been explained by their self-ionisation:^{57, 58}



Iodine tris(sulfonates) have also been studied by nuclear quadrupole resonance (NQR) spectroscopy and Mössbauer spectroscopy.⁵⁹ The results of these studies together with X-ray diffraction data for a related structure, tris(acetato)iodine(III) $\text{I}(\text{OCOCH}_3)_3$, imply that these compounds, like other derivatives of trivalent iodine, have T-shaped configurations.⁵⁹

The spectral characteristics of interhalogen fluorosulfates and interhalogen triflates, which are derivatives of trivalent iodine, make it possible to conclude that the geometries of their molecules are identical to those of other compounds of this class.^{49, 60}

The tentative inferences about the structures of iodosyl and iodyl sulfonates are based on some of their physicochemical properties. The fact that iodosyl and iodyl derivatives are insoluble in the corresponding acids is strong evidence for their polymeric structures.^{61, 62} The associated structure of iodosyl and iodyl sulfonates, postulated by Dasent and Wadington,⁶³ may be due to bridge binding of sulfonate groups or to the formation of chains consisting of $-\text{I}-\text{O}-\text{I}-$ fragments. This type of association is also supported by the Raman spectrum⁶³ of the iodyl fluorosulfate $(\text{O}_2\text{I})\text{SO}_3\text{F}$ (**3**), which does not dissociate to give O_2I^+ and SO_3F^- ions. The fact that the absorption band of the O_2I group is shifted by 50 cm^{-1} to shorter wavelengths points to a polymeric structure of this compound. The vibrational spectra of iodyl and iodosyl sulfonates also point to a polymeric structure of these compounds. In particular, the presence of a vibration band at 650 cm^{-1} in the spectrum of iodosyl fluorosulfate $(\text{OI})\text{SO}_3\text{F}$ (**4**) indicates that the OI groups are strongly associated and that $-\text{I}-\text{O}-\text{I}-$ chains are formed. In addition, the spectrum of this compound contains bands at 1350 , 1150 and 1000 cm^{-1} corresponding to vibrations of the SO_3 fragment. The two former frequencies are typical of bidentate bridging SO_3 groups, while the latter frequency, which is the lowest, is characteristic of monodentate SO_3 groups.⁶² Based on the spectral parameters of iodosyl trifluorosulfate and on the known structural features of other derivatives of polyvalent iodine, it can be assumed that the molecule of the compound **4** is a trigonal bipyramid, in which the base is formed by one oxygen atom and two lone electron pairs and the axial positions are occupied by the oxygen atoms of the fluorosulfate group.

Among polymeric iodine sulfates and sulfonates, only iodosyl sulfate $(\text{OI})_2\text{SO}_4$ (**5**) has been studied by X-ray diffraction analysis.⁶⁴ The results of this study indicate that this compound has a layered structure (sandwich-like layers parallel to the 001 plane). Each layer, in turn, consists of infinite helical chains (OI) linked to one another through SO_4 tetrahedra (Fig. 2). It should be noted

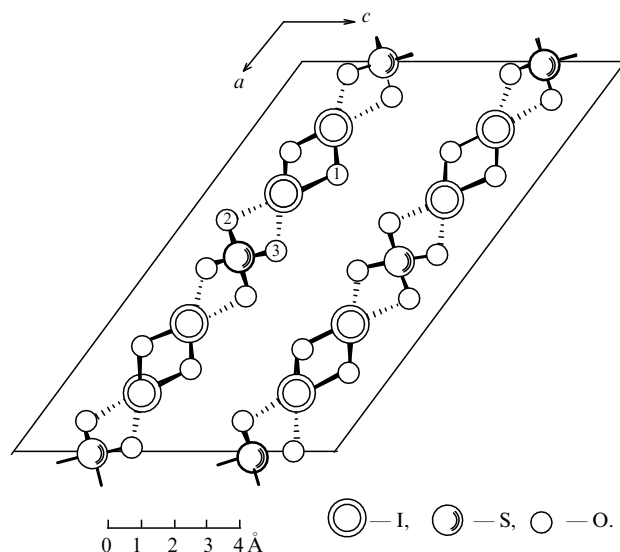


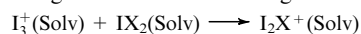
Figure 2. Projection of the polymeric chain in $(\text{OI})_2\text{SO}_4$ along the 010 plane.

that the same structure for the compound **5** has been proposed⁶³ based on its vibrational spectra.

If the two lone electron pairs are taken into account, the overall geometry of bonds surrounding the iodine atom is a distorted trigonal bipyramid, the iodine atom being located at its centre. The four oxygen atoms lie in the equatorial plane, while the two lone pairs occupy the axial positions. The $\text{I}-\text{O}$ bond lengths are dissimilar, namely: $\text{I}-\text{O}(1)$ 1.97 , $\text{I}-\text{O}(2)$ 2.53 and $\text{I}-\text{O}(3)$ 2.42 Å .

The molecular structure of the iodosyl sulfate **5** accounts for its instability with respect to water. Water molecules easily attack the SO_4 groups to give H_2SO_4 , the IO group being converted into I_2O_3 .⁶⁴

Valuable information about the reactivity of inorganic sulfonates can be obtained by studying their electrolytic dissociation. Study of the electrical conductivities of solutions of fluorosulfates, triflates and sulfates in concentrated sulfuric acid has shown that the majority of sulfonate derivatives dissociate in solution.^{65–67} It has also been found that in solution in trifluoromethanesulfonic acid, the fluorosulfate ligand in iodine tris(fluorosulfate) $\text{I}(\text{OSO}_2\text{F})_3$ **6** is readily replaced by a triflate ligand.⁶⁷ Fluorosulfonic (HSO_3F) and pyrosulfuric ($\text{H}_2\text{S}_2\text{O}_7$) acids have been found to be suitable solvents for iodine(III) interhalogen fluorosulfates.^{50, 60} Conductometric and spectroscopic studies of solutions of these compounds in the above acids indicate that iodine sulfates completely dissociate into ions and that dissociation is accompanied by quantitative formation of solvated cations $\text{IX}_2^+(\text{Solv})$ and $\text{I}_2\text{X}^+(\text{Solv})$. Study of the behaviour of solutions and melts of an equimolar mixture of $\text{I}_3\text{OSO}_2\text{F}$ (**7**) and $\text{IX}_2\text{OSO}_2\text{F}$ shows that exchange between the halide ligands occurs in these systems.



$\text{X} = \text{Cl}, \text{Br}$.

The ionic nature of the iodine–ligand bonds has also been confirmed by X-ray diffraction data,^{45, 64} which indicate that, whereas in organic sulfonates of trivalent iodine an increase in the nucleofugal capacity of the ligand results in an increase in the degree of ionicity of the bond (*i.e.* in an elongation of the $\text{I}-\text{O}$ bond), the $\text{I}-\text{O}$ bond (2.47 and 2.53 Å ⁶⁴) in iodosyl sulfate **5** is longer than the $\text{I}-\text{O}$ bond in iodine fluorosulfate **1** by approximately 0.2 Å , although the fluorosulfate group exhibits super-nucleofugal capacity. This seeming anomaly may be due to the fact that the iodine atom in the fluorosulfate **1** is bound to two oxygen atoms, whereas the iodine atom in the compound **5** (owing to the polymeric structure of iodosyl sulfate) is linked to four

oxygen atoms. Therefore, it may be expected that iodosyl sulfate would be a stronger electrophile than iodine fluorosulfate.

Thus, the data on the structures of inorganic sulfate and sulfonate derivatives of polyvalent iodine indicate that there is a clear-cut relationship between the nature of the ligands at the iodine atom and the structure of a particular derivative. It can be expected that the reactivity and physicochemical properties of these compounds would depend on the nature and the number of ligands and, in particular, that their electrophilicity would increase with an increase in the number and nucleofugal properties of sulfonate and sulfate residues.

III. Methods for the synthesis of sulfonates and sulfates of polyvalent iodine

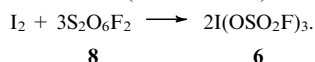
The fairly intense development of the chemistry of this class of compound has resulted in the appearance of diverse methods for their synthesis most of which have been surveyed in reviews^{68–70} published in 1970 and 1974. However, the progress achieved in recent years has scarcely been surveyed, and in the recent review,⁷¹ methods for the synthesis of iodine sulfonates received little attention. We have attempted to fill this gap.

1. Iodine fluorosulfates

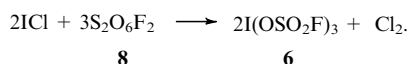
In most cases, various iodine sulfonates are synthesised by specific methods. Peroxydisulfuryl difluoride **8** proved to be the most convenient starting compound for the synthesis of iodine, chlorine and bromine fluorosulfates.⁷² Although **8** belongs to the class of peroxides, it differs from most of the known peroxides in that it is completely non-explosive and quite stable in the isolated state.²⁵

Since peroxydisulfuryl difluoride easily dissociates into relatively stable free radicals, the majority of reactions of this compound (including interaction with halogens) apparently involve fluorosulfate radicals.^{73,74} The reaction of the peroxide **8** with a halogen affords various fluorosulfates of this halogen. In 1959, the first halogen fluorosulfate — fluorine fluorosulfate — was prepared in this way.⁷⁵ The first iodine fluorosulfate was obtained from another compound, namely, silver fluorosulfate.⁷⁶ However, since this starting compound is too expensive, this method has not found practical application, and later, iodine fluorosulfate has been mostly obtained using peroxydisulfuryl difluoride.⁷⁷

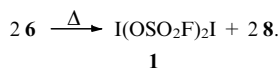
The reaction of iodine with excess peroxydisulfuryl difluoride gives iodine tris(fluorosulfate) **6** in a good yield.⁵⁸



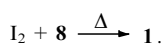
The main advantage of this method is that the resulting product requires no purification; only excess peroxide should be removed *in vacuo*. Iodine tris(fluorosulfate) is a non-volatile solid (m.p. 32 °C), which is hydrolysed fairly readily with water.⁷⁸ It can also be obtained by the reaction of the peroxide **8** with iodine chloride.⁷²



Another widely used fluorosulfate, the compound **1**, was prepared for the first time in 1965 by thermal decomposition of iodine tris(fluorosulfate).⁴⁹

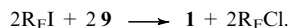
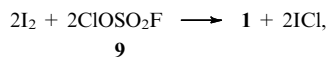


The compound **1** is a non-volatile diamagnetic solid.⁴⁹ An alternative and a more convenient method for the synthesis of iodine fluorosulfate **1** consists in the oxidation of iodine with an equimolar amount of peroxydisulfuryl difluoride with heating.⁴⁹

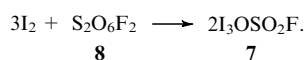


When the reactants are taken in equimolar amounts, iodine fluorosulfate **1** is formed as the major reaction product. However, in addition to the compounds **1** and **6**, other iodine fluorosulfates of the composition $\text{I}_n\text{OSO}_2\text{F}$ are also formed in the $\text{I}_2\text{--S}_2\text{O}_6\text{F}_2$ system; this will be discussed below.

Not long ago, yet another method for the synthesis of the compound **1** has been proposed.⁷⁹ It involves oxidation of elemental iodine or perfluoroalkyl iodides with a milder oxidising agent, chlorine fluorosulfate ClOSO_2F (**9**).



The reaction of peroxydisulfuryl difluoride **8** with excess iodine gives rise to triiodine monofluorosulfate **7**.⁴⁹



A high yield of the product is achieved when iodine is taken in a slight excess with respect to its stoichiometric amount and the reaction mixture is slowly heated to 85 °C. Triiodine monofluorosulfate **7** is a hygroscopic solid; it melts at 92 °C with evolution of iodine.

Study of the magnetic, cryoscopic and spectral properties of the $\text{I}_2\text{--S}_2\text{O}_6\text{F}_2$ system has shown that, depending on the mole fraction of the peroxydisulfuryl difluoride present, several iodine fluorosulfates can be formed in the system.⁸⁰ The results of this study are presented as the dependence of the melting point of the system on the mole fraction of the compound **8** (Fig. 3). The maxima in this plot correspond to various iodine fluorosulfates. In particular, the researchers identified $\text{I}_7\text{OSO}_2\text{F}$, $\text{I}_3\text{OSO}_2\text{F}$ (**7**), $\text{I}(\text{OSO}_2\text{F})_2\text{I}$ (**1**), and $\text{I}(\text{OSO}_2\text{F})_3$ (**6**). Molecular weights of the components were determined by cryoscopy.

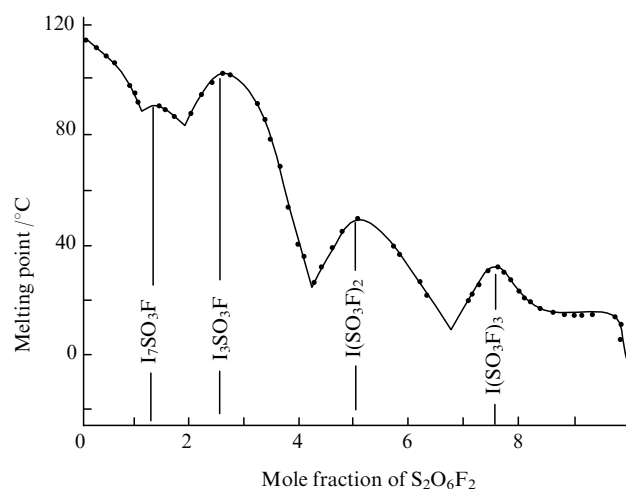
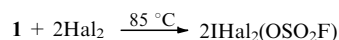
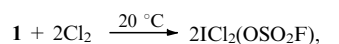


Figure 3. The $\text{I}_2\text{--S}_2\text{O}_6\text{F}_2$ system.

Another frequently encountered class of fluorosulfates of trivalent iodine comprises interhalogen fluorosulfates. These compounds can be synthesised using two approaches: direct introduction of a halogen or an interhalogen into the molecule of iodine trifluorosulfate⁵⁰ and the replacement of halide ligands at the iodine atom in a iodine interhalogen fluorosulfate or of two iodine atoms in triiodine monofluorosulfate by other halogens.^{50,81}

The former method has synthetic limitations. The reaction with chlorine occurs spontaneously at room temperature, whereas the reactions with bromine and iodine are initiated by heating the mixture to 85 °C.



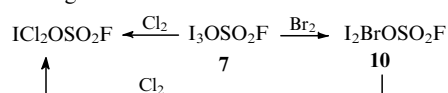
Hal = Br, I.

Solid reaction products slowly crystallise out of the melt, and excess halogen is easily distilled off upon evacuation of the mixture cooled below room temperature. However, in the case of interhalogen derivatives ICl and IBr, which act as ionising solvents, it is very difficult to isolate solid crystalline products from a viscous solution containing an excess of an interhalogen compound.

An attempt to prepare diiodobromine fluorosulfate $\text{I}_2\text{BrO-SO}_2\text{F}$ (**10**) by the addition of elementary iodine to bromine fluorosulfate failed. The reaction yielded the compounds **1** and **7**.⁶⁰ In those cases where the reaction mixture was kept at room temperature, bromine volatilised, and the excess of the reagent formed a complex with the iodine fluorosulfate **1**.

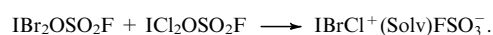
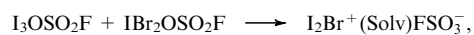
Thus, if the halogen in the Hal_2 molecule is more electron-withdrawing than the halide ligands at the iodine atom in the interhalogen compound, the reaction yields new interhalogen fluorosulfates. Otherwise, substitution of the halogen in $\text{Hal}(\text{O-SO}_2\text{F})_2\text{Hal}$ occurs.

The second approach to the synthesis of iodine(III) interhalogen fluorosulfates by the replacement of halide ligands at the iodine atom is used more frequently.⁶⁰ The compounds **7** and **10** have been used as the initial compounds for the synthesis of various interhalogen derivatives. Some examples of these reactions are given below.

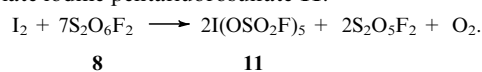


As in the case of addition, in this case, too, the higher electronegativity of the halogen atom entering the molecule compared to that of the halogen atom being displaced is the main driving force of the process. These reactions might occur *via* intermediates such as $\text{IX}_2\text{X}'_2\text{SO}_3\text{F}$, where $\text{X} = \text{I}$ or Br and $\text{X}' = \text{Cl}$ or Br . However, no experimental data supporting the existence of these intermediates have been obtained. In our opinion, this is due to their low stability.

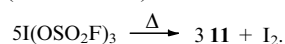
The results of a study of the UV spectra and electrical conductivities of molten mixtures of symmetrical poly- and interhalogen fluorosulfates or their solutions in strong acids indicate the formation of non-symmetrical interhalogen cations. The similarity of the halogen exchange reactions in solutions and melts is due to the fact that in both cases, ionic dissociation of substrates occurs. The outcome of the exchange reactions is determined by the entropy and enthalpy factors, and they are favourable for the formation of a thermodynamically more stable non-symmetrical cation rather than of a symmetrical cation.



Oxidation of iodine with peroxydisulfuryl difluoride **8** results most typically in trivalent iodine. However, heating of the reaction mixture to 90–130 °C and the use of an excess of the peroxide **8** (the molar ratio of the reactants was 1 : 7) made it possible⁴⁹ to isolate iodine pentafluorosulfate **11**.



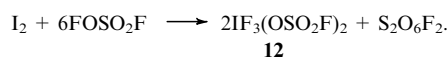
The same compound is formed in the pyrolysis of iodine tris(trifluorosulfate) **6**.⁴⁹



Iodine pentafluorosulfate was obtained by treatment of another fluorosulfate derivative of pentavalent iodine, namely, iodine trifluorobis(fluorosulfate) **12**, with sulfur trioxide.⁴⁹

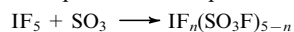


Iodine trifluorobis(fluorosulfate) needed for this synthesis can be prepared by the reaction of iodine with an excess of fluorine fluorosulfate at room temperature.⁸²



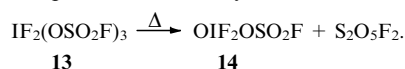
After removal of the peroxide and excess hypofluorite, the product **12** is obtained in a quantitative yield. As should be expected, the ¹⁹F NMR spectrum of the iodine trifluorobis(fluorosulfate) **12** points to two types of the environment of the fluorine atom. At 25 °C, the fluorine atoms bound to iodine are responsible for a broad band, which splits below –10 °C into two peaks in a ratio of 2 : 1.⁸² The non-equivalence of the fluorine atoms is not manifested for the *cis*- and *trans*-isomers of iodine trifluorobis(fluorosulfate), which is in agreement with the tetragonal bipyramidal structure proposed for **12**.

Recently, it has been found that compound **12** and its analogues of the general formula $\text{IF}_n(\text{OSO}_2\text{F})_{5-n}$ can be obtained by insertion of sulfur trioxide into the I–F bond in iodine pentafluoride.⁸³ Moreover, by varying the molar ratio of the starting compounds, the reaction can be directed at the preparation of a particular compound of this group.



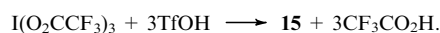
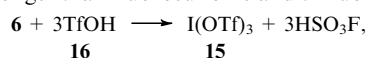
$n = 0 - 5$.

Thermolysis of one of these compounds, namely, iodine difluorotris(fluorosulfate) $\text{IF}_2(\text{OSO}_2\text{F})_3$ **13**, was found to yield the compound described by the formula $\text{OIF}_2\text{OSO}_2\text{F}$ **14**.

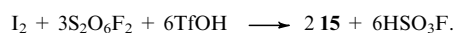


2. Iodine triflates

There are no direct methods for the synthesis of iodine triflates except for the synthesis of iodosyl and iodyl triflates, which is considered below in the section devoted to iodosyl and iodyl sulfonates. Therefore, iodine triflates are prepared by exchange reactions between derivatives of trivalent iodine, incorporating residues of oxygen-containing acids, with trifluoromethanesulfonic acid, which displaces anions of weaker acids from these iodine derivatives. For example, the synthesis of iodine tris(triflate) **15** from the tris(fluorosulfate) **6** and iodine tris(trifluoroacetate) is based on the fact that trifluoromethanesulfonic acid **16** is stronger than fluorosulfonic and trifluoroacetic acids.^{59, 67}



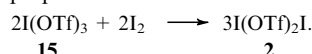
Iodine tris(triflate) **15** can also be obtained *in situ* by the reaction of iodine with peroxydisulfuryl difluoride without isolation of the intermediate iodine tris(trifluorosulfate).⁶⁷



These reactions do not give mixed compounds of the $\text{I}(\text{OSO}_2\text{F})_x(\text{OTf})_{3-x}$ type, because iodine tris(triflate) **15** is soluble only in trifluoromethanesulfonic acid, and the corresponding fluorosulfate is soluble in HOSO_2F and HOTf .

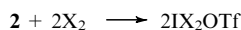
Iodine tris(triflate) **15** is a white hygroscopic solid melting at 119 °C; it is stable during heating to 170 °C *in vacuo*.

At present, the reaction of iodine tris(triflate) with an equimolar amount of iodine still remains the only plausible method for the preparation of iodine monotriflate **2**.⁶⁷



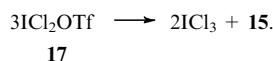
Iodine triflate **2** is a brown hygroscopic solid, m.p. 122 °C. On heating above 170 °C, it decomposes.

Interhalogen triflates, like interhalogen fluorosulfates, are formed in the oxidative addition of halogens to the iodine triflate **2**.⁵⁰



X = Cl, Br, I.

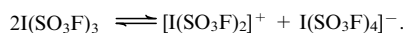
Despite the fact that various halogens can enter into this reaction, only the product of addition of bromine has been isolated in a pure state so far.⁵⁰ Spectroscopic studies have shown that dichloroiodine(III) triflate **17** is very unstable and readily decomposes.



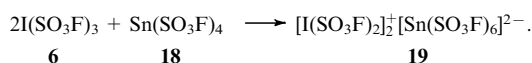
Iodine adds to molten iodine triflate **2**; however, the reaction product has not been isolated;⁶⁷ apparently, this is due to the fact that triiodine triflate $\mathbf{I}_3\mathbf{OTf}$ decomposes at this temperature.

3. Complex salts of iodine tris(sulfonates)

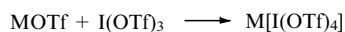
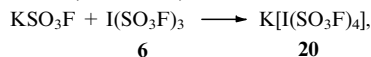
As noted above, iodine sulfonates are self-ionised in solutions of the corresponding acids. This is a rationale of the amphoteric properties of iodine sulfonates.



The basic properties of iodine tris(fluorosulfate) **6** are manifested in its reaction with tin tetrafluorosulfonate **18** in peroxydisulfuryl difluoride.⁶⁵ This reaction results in the formation of a bright yellow complex salt **19**.



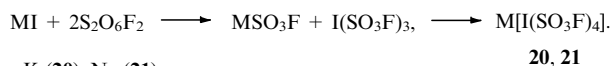
At the same time, in the reactions with alkali metal sulfonates, iodine tris(sulfonates) behave as acids.^{65, 67}



M = K, Rb, Cs.

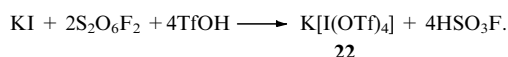
These reactions are fairly convenient for the synthesis of iodine tetrakis(sulfonate) derivatives.

An alternative method for the preparation of the complex salt **20** and its sodium analogue **21** is the reaction of sodium (or potassium) iodide with excess peroxydisulfuryl difluoride **8** at room temperature.^{84, 85} In these reactions, iodine is oxidised to the trivalent state instead of being displaced from the molecule. The researchers believe that the corresponding metal fluorosulfonates $\mathbf{MSO}_3\mathbf{F}$ (M = Na, K) are formed initially, and then they are converted into the complex salts $\mathbf{M}[\mathbf{I}(\mathbf{SO}_3\mathbf{F})_4]$ **20** and **21**.

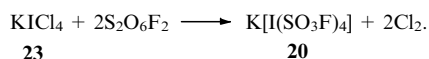


M = K (**20**), Na (**21**).

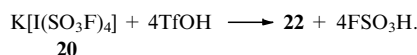
Tetracoordinated triflate iodates **22** are formed upon oxidation of alkali metal iodides with peroxydisulfuryl difluoride in trifluoromethanesulfonic acid.⁶⁷



Yet another method for the synthesis of complex sulfonates is ligand exchange at a tetracoordinated iodine atom. In this case, potassium tetrachloroiodate **23** serves as the initial compound for the preparation of the salt **20**.⁸⁵



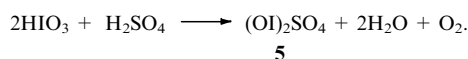
A similar triflate salt **22** can be obtained by the replacement of the fluorosulfate group by a triflate group in the reaction of the salt **20** with an excess of trifluoromethanesulfonic acid **16**.⁶⁷



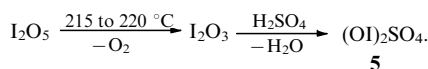
4. Iodosyl and iodyl sulfonates and sulfates

Analysis of various types of iodine sulfonates presented in Table 1 makes it possible to conclude that iodosyl and iodyl sulfonates are the most abundant type of compound among the derivatives in question. Therefore, it is expedient to consider in a separate Section the methods for synthesis of iodosyl sulfonates, which are I(III) derivatives containing an OI group, and iodyl sulfonates, which are I(V) derivatives containing an O₂I group.

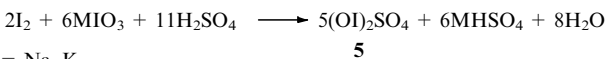
The first attempts to synthesise iodosyl sulfonates date back to the late XIX century. As has already been noted, the first representative of this class, iodosyl sulfate (**5**, the Chrétien reagent), was obtained as early as 1898 by thermal decomposition of iodic acid in concentrated sulfuric acid.⁸⁶



Later, iodosyl sulfate **5** was prepared[†] by heating iodine pentoxide in concentrated sulfuric acid.⁸⁷ The researchers believe that in the first stage, the oxide $\mathbf{I}_2\mathbf{O}_5$ decomposes to $\mathbf{I}_2\mathbf{O}_3$. Iodine trioxide, which possesses basic properties, reacts, in its turn, with sulfuric acid to give iodosyl sulfate **5**.



More recently, iodosyl sulfate has been prepared using a redox reaction between elementary iodine and sodium (or potassium) iodate in concentrated sulfuric acid.⁸⁸

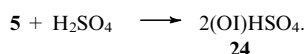


M = Na, K.

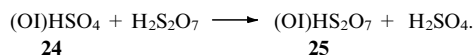
Concentrated nitric acid was also used as the oxidising agent for the synthesis of iodosyl sulfate **5**.⁸⁸



Iodosyl sulfate **5** reacts with sulfuric acid to give iodosyl hydrogensulfate **24**.⁷⁰

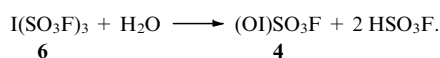


The compound **24** is unstable; in the opinion of the researchers cited,⁷⁰ it polymerises. It can serve as the initial compound in the synthesis of one more derivative of trivalent iodine, namely, iodosyl hydrogenpyrosulfate **25**.



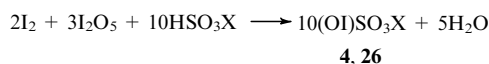
Based on conductometric and spectroscopic studies, it was proposed that, unlike the initial iodosyl hydrogensulfate **24**, the compound **25** is ionic.⁷⁰

Iodosyl fluorosulfate **4** was synthesised for the first time in 1960 by the hydrolysis of iodine tris(fluorosulfate).⁵⁸



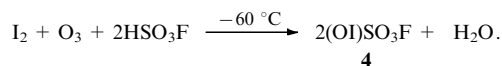
Later, its structure and properties were studied.⁶² This compound and related iodosyl triflate **26** were prepared by the reaction of iodine with iodine pentoxide and the corresponding acid.⁶²

[†] In the same study,⁸⁷ the structure of iodosyl sulfate was determined for the first time.

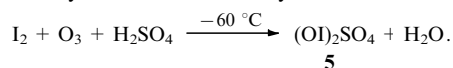


X = F (**4**), CF₃ (**26**).

In 1980, a new method for the preparation of iodosyl fluorosulfate **4** was proposed. The method consists in the oxidation of iodine with ozone in the corresponding acid under mild conditions.⁸⁹

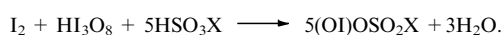
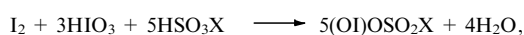


Iodosyl sulfate **5** was also synthesised in this way.



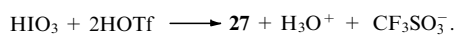
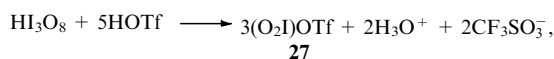
However, the heavy drawbacks of this method associated with the use of gaseous ozone preclude its adaptation as a preparative procedure.

Sulfonate iodosyl derivatives are also formed when HIO₃ or HI₃O₈ is used instead of iodine pentoxide.^{62, 87}

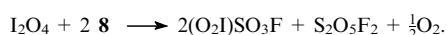
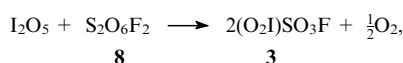


X = F, CF₃.

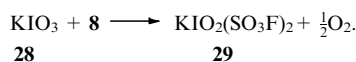
When the two latter reactions are carried out in trifluoromethanesulfonic acid and without iodine, they afford iodyl triflate **27** rather than iodosyl triflate **26**.⁶²



The corresponding iodyl fluorosulfate **3** can formally be regarded as the product of insertion of sulfur trioxide into the I–F bond of iodyl fluoride O₂IF. Unfortunately, the attempt to synthesise iodyl fluorosulfate in this way was unsuccessful;⁹⁰ however, this derivative can be obtained relatively easily by the reaction of peroxydisulfuryl difluoride **8** with iodine penta- and tetraoxides.⁹⁰

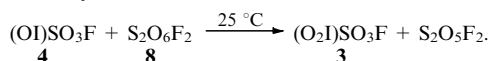


At the same time, the reaction of the peroxide **8** with potassium iodate gives rise to compound **29**.⁶¹

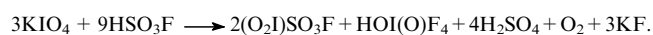


The Raman spectra of **29** indicate that this compound is a stoichiometric mixture of potassium fluorosulfate and iodyl fluorosulfate. This implies that, unlike iodine tris(fluorosulfate) which forms complex salts, iodyl fluorosulfonate does not accept the fluorosulfate group.⁶¹

Oxidation of iodosyl fluorosulfate **4** with the peroxide **8** affords iodyl fluorosulfate **3**.⁶²

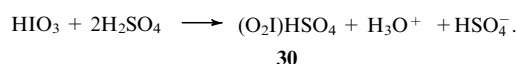


An alternative method for the preparation of iodyl fluorosulfate is based on the interaction of potassium metaperiodate with fluorosulfonic acid.⁹¹



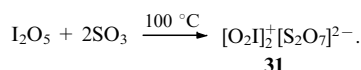
To the best of our knowledge, no data on the synthesis of iodyl sulfates have been reported, whereas iodyl hydrogensulfate **30** has

been thoroughly studied. The latter compound has been synthesised by heating iodic acid in concentrated sulfuric acid.⁹²

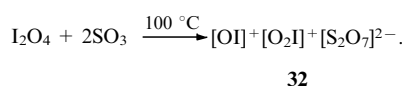


Like iodyl and iodosyl sulfonates, iodyl hydrogensulfate **30** is polymeric. However in a highly dilute solution in sulfuric acid, this compound exists as the solvated monomer (O₂I)HSO₄·H₂SO₄.⁹³ When the concentration of the solution increases, the solvent molecule is eliminated from the solvate, and the iodyl fragments are joined together yielding polymeric chains.⁹³

Apart from iodyl hydrogensulfates, iodyl pyrosulfate **31** is also known. This derivative is readily formed upon heating of iodine pentoxide with liquid sulfur trioxide.⁹⁴



Iodyl pyrosulfate **31** can also be obtained by the reaction of liquid sulfur trioxide with potassium or tin iodate. However, when I₂O₄ was introduced into this reaction, it resulted in the formation of a mixed salt — iodosyl iodyl pyrosulfate **32**.⁹⁴



IV. Reactions of sulfonates and sulfates of polyvalent iodine

Sulfonates and sulfates of polyvalent iodine, synthesised about a century ago, have only recently attracted the attention of organic chemists as extremely reactive compounds; in some cases, the use of these reagents makes it possible to accomplish some transformations that have previously been impossible. These compounds are especially useful owing to two characteristic features of their chemical behaviour. Firstly, they are efficient oxidants and, secondly, the iodine atom in them exhibits clear-cut electrophilic properties in reactions with various organic substrates. By varying the oxidation state of the iodine atom and the nature of heteroatomic ligands, one can change substantially the particular manifestation of these properties and thus control the reactivity of sulfonates and sulfates.

Valuable information about the reactivity of iodine sulfonates could be obtained from a systematic consideration of the published data on the reactions of these compounds with alkyl halides, alkenes and aromatic compounds. Unfortunately, no systematic studies on the reactions of sulfonates with these substrates have been carried out. The available data are fairly scattered and mostly refer to the reactions of iodosyl sulfonates, iodine fluorosulfate and iodine tris(fluorosulfate). In fact, in the detailed reviews by Fokin *et al.*^{25, 71} devoted to synthetic applications of halogen fluorosulfates, reactions of iodine fluorosulfates are considered only cursorily.

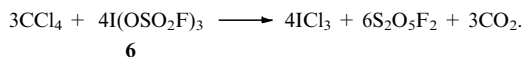
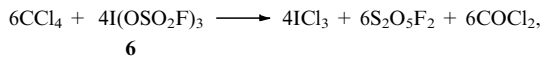
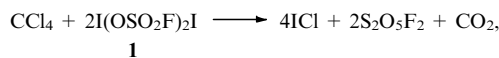
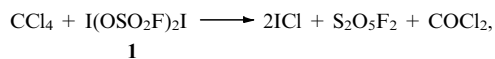
Therefore, we attempted to classify the published data on this topic according to the type of reactions of iodine sulfonates and sulfates with unsaturated and aromatic compounds and with alkyl halides, in order to identify the common features of these reactions as functions of the nature of heteroatomic ligands at the iodine atom and its oxidation state.

1. Oxidative dehalogenation

Before we discuss the reactions of oxidative dehalogenation, we would like to emphasise that no data on this type of reaction have been reported for iodine triflates and sulfates, whereas oxidative dehalogenation of alkyl halides with iodine fluorosulfates has been studied fairly comprehensively.

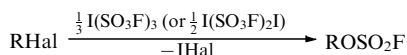
In 1965, it was found that iodine fluorosulfate **1** and iodine tris(fluorosulfate) **6** vigorously react with carbon tetrachloride at room temperature.⁴⁹ Depending on the molar ratio of the sub-

strates, CCl_4 can be oxidised stepwise to give phosgene or carbon dioxide.



Iodine fluorosulfate equally readily oxidises chloroform and trichlorofluoromethane.⁴⁹ In addition to phosgene, carbon dioxide and fluorosulfonic anhydride, these reactions yield molecular chlorine. Iodine fluorosulfate **1** was found to react efficiently with pyridine to give a yellow hygroscopic solid.⁴⁹ However, the researchers were not able to identify the unstable products of the reaction. Iodine monofluorosulfate and tris(fluorosulfate) are less reactive towards fluorinated haloalkanes than fluorosulfates of other halogens. They do not react with dichlorodifluoromethane, trichlorotrifluoroethane or with primary perfluoroalkyl bromides.^{95, 96}

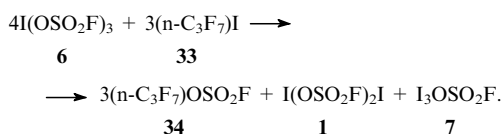
However, iodine monofluorosulfate and iodine tris(fluorosulfate) react relatively readily with non-fluorinated alkyl halides.⁹⁶



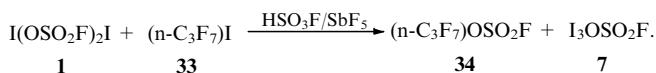
R = Me, Et; Hal = Cl, I.

(Triiodine monofluorosulfate has been found to be inert in all these reactions.⁷¹)

Iodine tris(fluorosulfate) **6**, as expected, is more reactive towards alkyl halides than iodine monofluorosulfate **1**, owing to the presence of three fluorosulfate ligands at the iodine atom. Thus the reaction of iodine tris(fluorosulfate) **6** with perfluoropropyl iodide **33** resulting in the replacement of the iodine atom by a fluorosulfate group occurs at 20–45 °C, whereas the same reaction involving iodine fluorosulfate **1** can be accomplished only under conditions of superacid catalysis in fluorosulfonic acid containing 15 mol.% of SbF_5 .



This process is accompanied by a slight exothermal effect.⁷¹

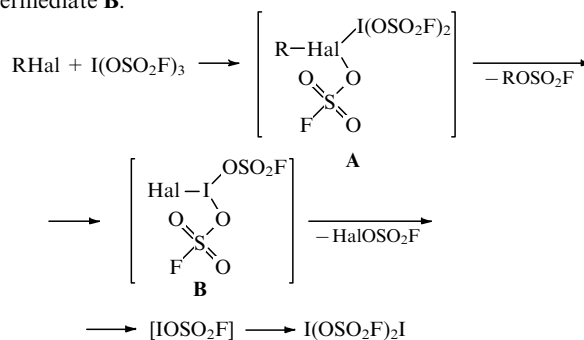


Based on experimental data, the researchers cited⁷¹ concluded that, in terms of their reactivity towards alkyl halides, iodine fluorosulfates can be arranged in the following series: $\text{I}(\text{SO}_3\text{F})_3 > \text{I}(\text{SO}_3\text{F})_2\text{I} > \text{I}_3\text{SO}_3\text{F}$. In other words, the activity of fluorosulfates decreases with a decrease in the number of fluorosulfate ligands.

A quantitative estimate of the oxidising ability of iodine fluorosulfates (based on the standard potentials established on platinum after it has been immersed into the compound under study) has shown that these reagents are among the strongest oxidants.⁹⁷ The results obtained in this study indicate that the above series for the reactivity of fluorosulfates in the oxidative dehalogenation coincides with the order of variation of their oxidising properties. Thus, it can be assumed that it is the oxidising capacity that determines the reactivity of fluorosulfates. This hypothesis is supported by the fact that the oxidising capacity

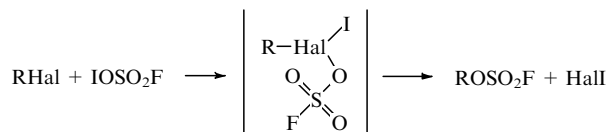
and the reactivity of iodine fluorosulfates in strongly acidic media (HSO_3F , $\text{HSO}_3\text{F}/\text{SbF}_5$) increase in parallel.

In the oxidative dehalogenation of RHal (Hal = Cl, I), iodine is more easily substituted by a fluorosulfate group than chlorine. An increase in the electron-withdrawing properties of groups attached to the same carbon atom as the leaving halogen atom retards the substitution of this atom by a fluorosulfate group.⁷¹ This provided grounds for assuming that during the replacement of halogen atoms in RHal , these atoms are oxidised with fluorosulfates to the trivalent state. The intermediate **A** thus formed decomposes to give the corresponding alkyl fluorosulfate and intermediate **B**.



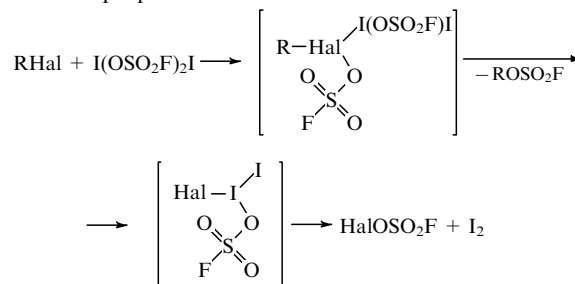
R = Me, Et; Hal = Cl, I.

Based on the wrong idea that iodine fluorosulfate is a hypoiodite derivative, Fokin *et al.*⁹⁷ proposed the following scheme for oxidative dehalogenation:



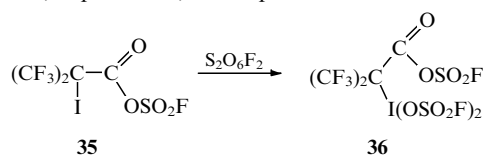
R = Me, Et; Hal = Cl, I.

However, in view of the actual structure of the iodine fluorosulfate, which is constituted as $\text{I}(\text{SO}_3\text{F})_2\text{I}$,⁴⁴ and by analogy with iodine tris(fluorosulfate) **6**, the following reaction mechanism can be proposed:



R = Me, Et; Hal = Cl, I.

This mechanism for the substitution of a fluorosulfate group for the halogen atom in alkyl halides is supported by the data obtained by the same researchers on the interaction of iodine tris(fluorosulfate) **6** with fluoroalkenes⁹⁸ and bis(trifluoromethyl) ketene⁹⁹ (see Section IV.2) as well as by the synthesis of stable organic iodosyl fluorosulfates by oxidation of perfluoroalkyl iodides, in particular, of compound **35**.¹⁰⁰

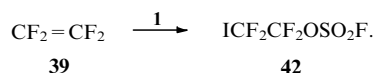
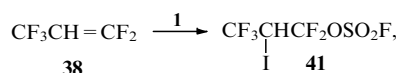
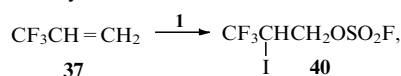


The adducts of type **36** formed in this reaction are syrupy yellow liquids, which are stable during storage (20 °C) and decompose on heating.¹⁰⁰

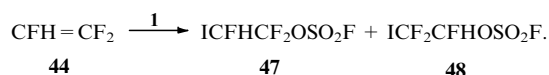
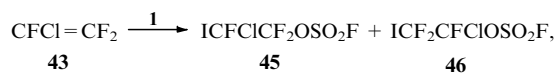
Thus, analysis of the published data demonstrates that iodine fluorosulfates are convenient reagents for the preparation of esters of fluorosulfonic acid. It is noteworthy that the behaviour of other iodine sulfonates in these reactions has scarcely been studied; however, their high reactivity suggests that the use of these reagents in the processes considered above would substantially extend the potentialities of oxidative dehalogenation of alkyl halides.

2. Addition to alkenes

Electrophilic addition of iodine sulfonates has been little investigated. However, the reactions of iodine fluorosulfate **1** and iodine tris(fluorosulfate) **6** with deactivated alkenes have been studied in considerable detail.^{45, 79, 101} For example, it has been shown¹⁰¹ that iodine fluorosulfate **1** reacts in Freon 113 with fluoropropenes **37** and **38** and with tetrafluoroethylene **39** to give β -iodoalkyl fluorosulfates **40–42**.

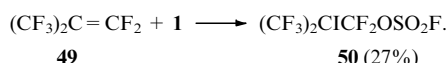


In these reactions, the addition products are formed regiospecifically, whereas in the reactions with chlorotrifluoroethylene **43** and trifluoroethylene **44**, mixtures of regioisomers have been obtained.⁴⁵

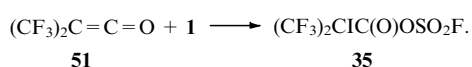


The reaction with trifluoroethylene **44** gives compound **47** as the major product (85%), which has been isolated in a pure state.⁴⁶ Unfortunately, the products of addition of iodine fluorosulfate **1** to chlorotrifluoroethylene **43** have identical boiling points, which precluded separation of regioisomers **45** and **46**.⁴⁵

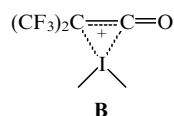
In the opinion of the researchers cited,⁴⁵ the course of the above reactions is markedly influenced by the fact that iodine fluorosulfate **1** is insoluble in Freon 113. This accounts for the relatively low reactivity of the compound **1** with respect to fluoroalkenes having less pronounced electrophilic properties. Thus the product of addition of iodine fluorosulfate **1** to octafluoroisobutene **49**, viz., compound **50**, was obtained only when the reaction mixture was kept for 3 weeks at 20–25 °C.⁴⁵



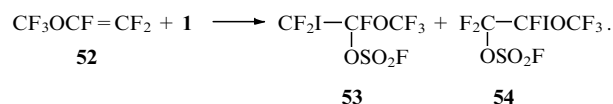
Iodine fluorosulfate **1** adds to perfluorinated cyclobutene⁴⁶ and cyclopentene⁴⁶ and readily reacts with highly electrophilic substrates such as bis(trifluoromethyl) ketene **51**.⁴⁵



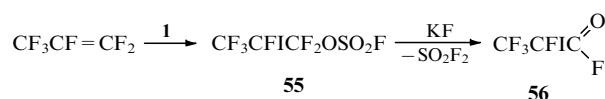
The ease of the reaction with the ketene **51** was attributed⁴⁵ to the tendency of iodine fluorosulfate **1** to form intermediate complexes of type **B**; this assumption implied an electrophilic mechanism of this reaction.



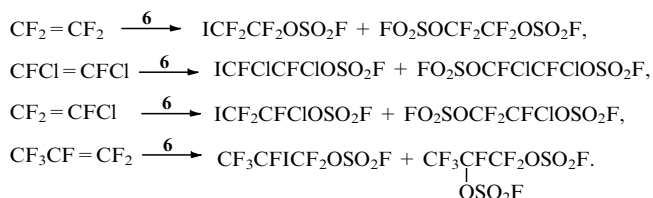
When iodine fluorosulfate **1** reacts with perfluorinated methyl vinyl ether **52**, compound **53** resulting from the atypical addition of the fluorosulfate at the multiple bond is formed as the major product, whereas only traces of the normal addition product **54** have been isolated.¹⁰²



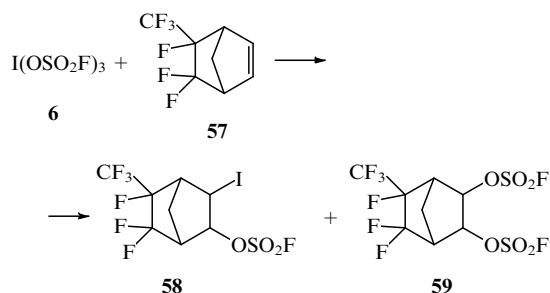
Adducts of iodine fluorosulfate with perfluoroalkenes are readily converted into acid fluorides.¹⁰² Recently, β -iodoperfluoropropyl fluorosulfate **55** has been converted into α -iodoperfluoropropionyl chloride **56**, which is a convenient intermediate for the manufacture of ion-exchange membranes.⁴⁷



Although the electrophilic properties of iodine tris(fluorosulfate) have been little studied, the available data indicate that it is more reactive than iodine fluorosulfate.⁹⁵ Iodine tris(fluorosulfate) **6** reacts with fluorinated derivatives of ethylene and propylene with heat evolution.⁹⁸ Its reactions with tetrafluoroethylene, 1,2-dichlorodifluoroethylene, chlorotrifluoroethylene and perfluoropropylene give rise to β -iodoalkyl fluorosulfates and perfluoroalkane-1,2-diyl bis(fluorosulfates), i.e. the products of formal addition of iodine fluorosulfate and peroxydisulfuryl difluoride at the double bond.^{98, 100}

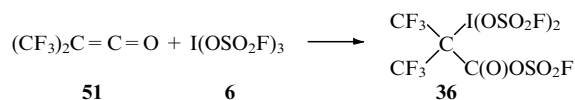


In order to elucidate the nature of the multiple bond in fluorine-containing bicycloheptenes, the reaction of iodine tris(fluorosulfate) **6** with the adduct formed by hexafluoropropene and cyclopentadiene **57** has been studied.¹⁰³ Despite the fact that the compound **6** is highly electrophilic, it adds at the double bond in bicycloheptene **57** without rearrangement to give 1,2-addition products. As in the case of acyclic perfluoroalkenes, the reaction affords iodo fluorosulfate **58** and bis(fluorosulfate) **59**.



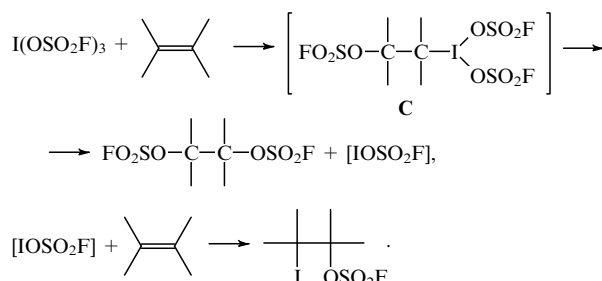
Important conclusions concerning the mechanism of this reaction could be drawn from the configurations of substituents in the reaction products. Unfortunately, the stereochemistry of the reaction was not studied.

The reaction of iodine tris(fluorosulfate) **6** with bis(trifluoromethyl)ketene **51** is of considerable interest. This reaction has permitted the synthesis of a stable organic iodosyl fluorosulfate **36**.⁹⁹

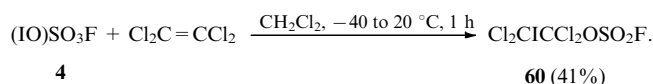


The stability of the compound **36** is due to the strong electron-withdrawing influence of the perfluoroalkyl and ester groups, which markedly hamper processes of nucleophilic substitution in this molecule.

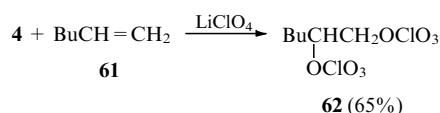
The latter reaction also seems to be of prime importance from the theoretical viewpoint. The fact that a stable product of 1,2-addition is formed in this reaction makes it possible to rationalise the formation of bis(fluorosulfates) and β -iodofluorosulfates in the reactions of iodine tris(fluorosulfate) **6** with alkenes.^{99, 100} It was assumed that these reactions involve type **C** intermediates, which are unstable and decompose to give a bis(fluorosulfonyloxy)alkane and iodine fluorosulfate. The latter adds to the excess of the alkene giving rise to β -iodo-fluorosulfate.⁹⁹



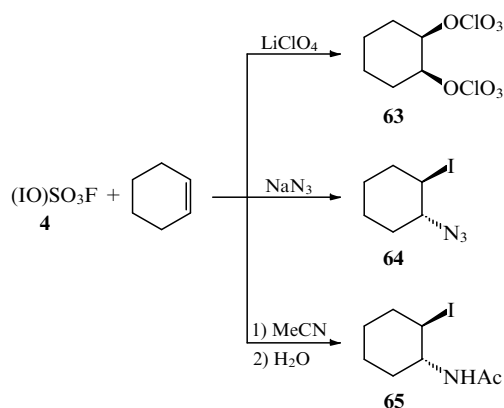
The authors of the present review have studied electrophilic addition of iodosyl fluorosulfate **4** to various alkenes.^{104–106} In the case of simple alkenes, these reactions occur vigorously and are accompanied by strong resinification. Normal addition products were obtained only for deactivated alkenes. For example, tetrachloroethylene reacts with iodosyl fluorosulfate **4** to give β -iodofluorosulfate **60**.¹⁰⁴



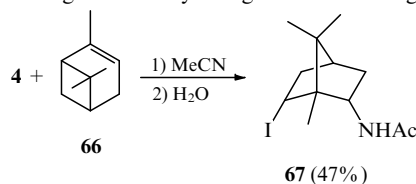
One of the possible ways of controlling the reactivity of iodosyl fluorosulfate **4** is to conduct the reactions with activated acyclic and cyclic alkenes in the presence of external nucleophiles. Thus the reaction of **4** with hex-1-ene **61** in the presence of lithium perchlorate results in the formation of bis(perchlorate) **62**.¹⁰⁴



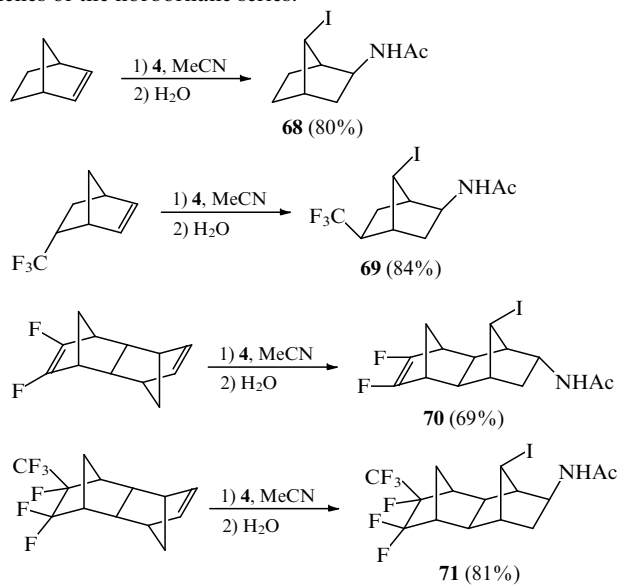
Stereochemical features of the addition of the reagent **4** to double bonds with the participation of external nucleophiles have been studied for the reactions with cyclohexene. If perchlorate anion is added as the nucleophile, the reaction affords 1,2-*cis*-diperchloroxy cyclohexane **63** in 61% yield;¹⁰⁴ if sodium azide is used instead of the perchlorate, 2-iodocyclohexyl azide **64** having the *trans*-configuration is formed.¹⁰⁴ When this reaction was carried out in acetonitrile, the product of conjugate addition, *trans*-iodoacetamide **65**, was obtained in a yield of 46%. In the presence of lithium perchlorate, in addition to the substituted acetamide **65** the yield of which increased under these conditions to 61%, diperchlorate **63** (15%) resulting from the competing addition of the nucleofugal perchlorate anion was isolated in a relatively low yield (15%).



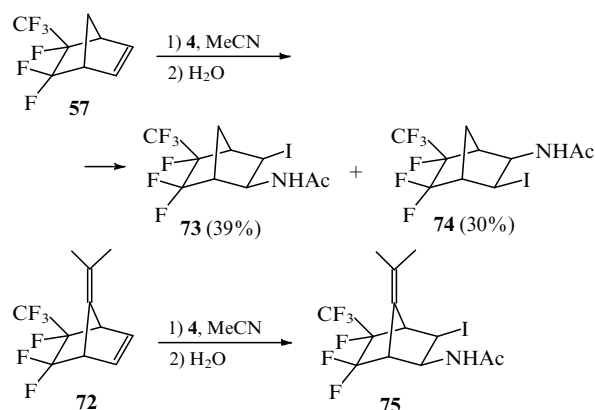
The addition of the reagent **4** to α -pinene **66** in acetonitrile occurs regioselectively and gives the rearranged acetamide **67**.¹⁰⁷



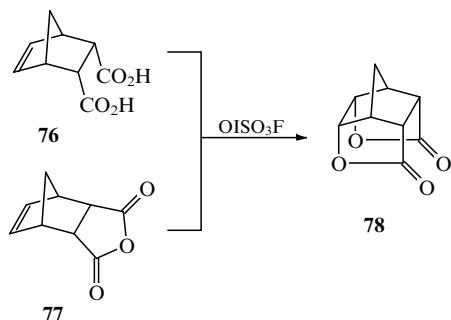
Other rearranged products, namely, compounds **68–71**, have been obtained by the reactions of iodosyl fluorosulfate **4** with alkenes of the norbornane series.^{104, 105, 108–110}



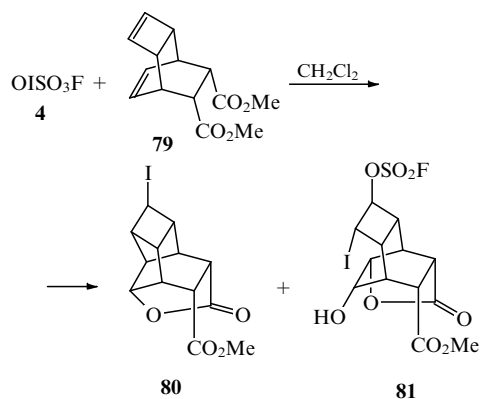
However, the reactions with the most deactivated fluoro-containing bicyclo[2.2.1]heptenes **57** and **72** afford 1,2-adducts **73–75** as the only products.^{105, 109, 110}



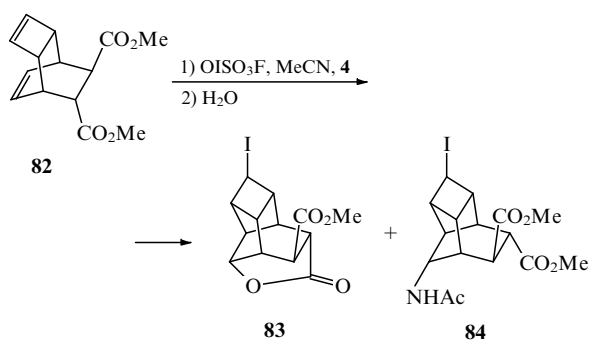
The reactions in which the addition of iodosyl fluorosulfate **4** to an unsaturated molecule is accompanied by ring closure are of particular interest.^{104, 111, 112} For example, norbornenedicarboxylic acid **76** and its anhydride **77** react with **4** to give bis- γ -lactone **78**. When the reaction with the acid **76** is carried out in acetonitrile, the yield of the lactone **78** is nearly quantitative.¹⁰⁴



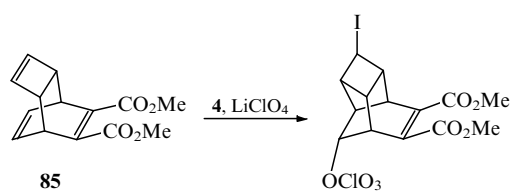
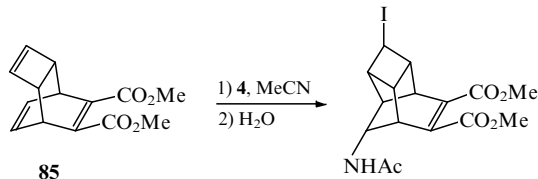
The reaction of the compound **4** with the cage diene **79** containing *cis*-arranged methoxycarbonyl groups in dichloromethane affords a mixture of two products, δ -lactone **80** and γ -lactone **81**.¹¹¹ When more polar acetonitrile is used as the solvent, δ -lactone **80** becomes the only reaction product.¹⁰⁴



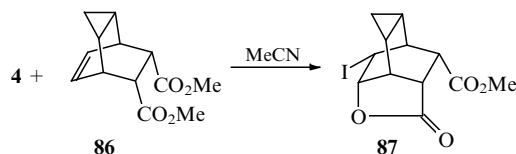
The reaction of iodosyl fluorosulfate with diene **82** containing *trans*-methoxycarbonyl groups in acetonitrile gives rise to δ -lactone **83** and amide **84**.¹⁰⁴



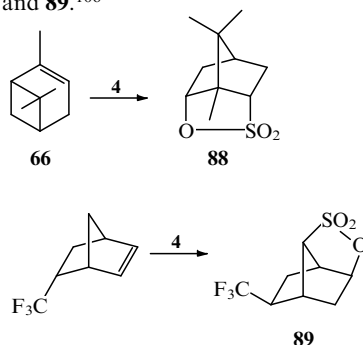
A similar reaction involving triene **85** the geometry of which precludes its lactonisation yields products of addition formed with the participation of external nucleophiles.



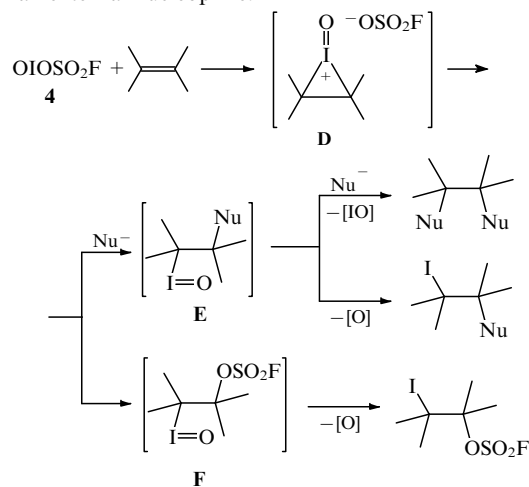
It is of interest that in the case of unsaturated cage ester **86** containing a cyclopropyl fragment, the attack is directed at the double bond, the three-membered ring being retained in the final product **87**.¹¹²



An alternative route for the transformations of iodosyl fluorosulfate, in particular, the transfer of its SO₃ fragment onto a double bond, was discovered when this reagent was made to react with α -pinene **66** and 5-*endo*-trifluoromethylnorbornene in ether without any additional nucleophiles. These reactions, which are accompanied by skeletal rearrangements and are highly stereo- and regio-selective, result in the formation of γ -sulfones **88** and **89**.¹⁰⁶

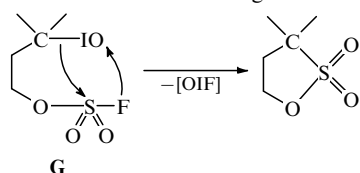


Based on these results, all the characteristic features of the reactions of iodosyl fluorosulfate **4** with alkenes can be interpreted in terms of a single mechanism. According to this mechanism, in the first step the double bond in the substrate is attacked by the iodosyl cation (the reagent **4**).¹⁰⁴ The subsequent opening of intermediate **D** can occur under the action of either the anion of **4** or an external nucleophile.



The formation of products of skeletal rearrangements in the case of bi- and polycyclic alkenes indicates that intermediate **D** is highly ionic and, hence, that iodosyl fluorosulfate is a strong electrophile. A distinctive feature of these processes is that most of the products contain an iodine atom rather than an iodosyl group. The elimination of oxygen from the intermediate iodosyl compounds of type **E** and **F** is due to the influence of excess alkene. This type of behaviour of iodosyl compounds has been established reliably for aromatic iodosyl derivatives.^{113–115} It can be assumed that aliphatic iodosyl compounds would behave similarly. The regioselectivity of reactions in the series of fluorine-containing norbornenes and α -pinene is controlled by electronic effects of the substituents.

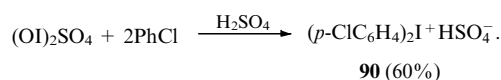
In the case where sultones are formed, the reaction occurs *via* compound **G**, which eliminates iodosyl fluoride. The formation of the OI–F bond is the driving force of this process.



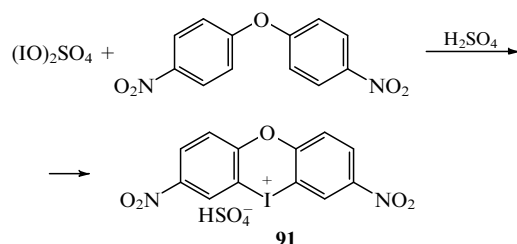
Thus, the reactions of iodosyl fluorosulfate with alkenes considered above indicate that this reagent, like iodine mono- and tris(fluorosulfates), is highly electrophilic. By varying the conditions of the reactions involving iodosyl fluorosulfate, one can control its reactivity, which makes it possible to transform alkenes into diverse derivatives.

3. Aromatic electrophilic substitution

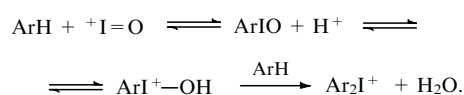
The ionic nature of the majority of sulfonate derivatives of polyvalent iodine accounts for their possible participation in aromatic nucleophilic substitution reactions. These reactions yield iodosylarenes, which are traditionally used in the synthesis of diaryliodonium salts.^{116–119} Therefore, the high reactivity of iodine sulfonates permits them to be used as convenient initial compounds for the preparation of diaryliodonium salts, which are efficient arylating reagents.^{120–122} In particular, treatment of chlorobenzene with iodosyl sulfate gives rise to diaryliodonium salt **90**.⁸⁸



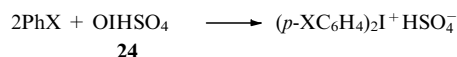
At the same time, when di(4-nitrophenyl) ether is introduced in this reaction, cyclic product **91** is formed.¹²¹



The formation of diaryliodonium hydrogensulfates has been explained⁸³ in the following way. Electrophilic attack by the iodosyl cation $^+\text{I}=\text{O}$ on the aromatic ring yields an intermediate iodosylarene derivative the condensation of which with a second molecule of the aromatic compound gives rise to the diaryliodonium salt.

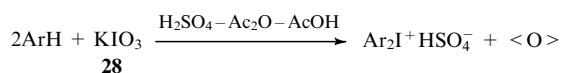


Diaryliodonium hydrogensulfates can also be obtained by using iodosyl hydrogensulfate **24**.⁹²

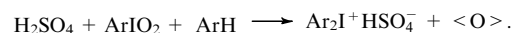
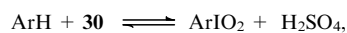
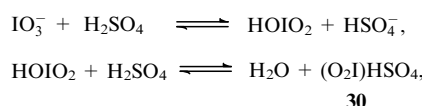


X = Alk, Hal.

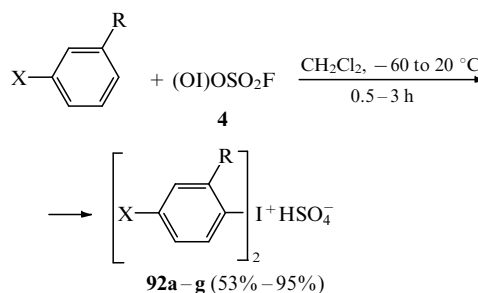
Diaryliodonium salts also arise in the reaction of potassium iodate **28** with aromatic substrates in the $\text{H}_2\text{SO}_4\text{--AcOH--Ac}_2\text{O}$ system.⁸⁸ This method is especially significant for the synthesis of salts containing electron-withdrawing substituents.



Although potassium iodate acts as an initial compound in this reaction, it was assumed⁸⁸ that diaryliodonium salts are formed by a mechanism that includes the *in situ* generation of iodyl hydrogensulfate **30**.



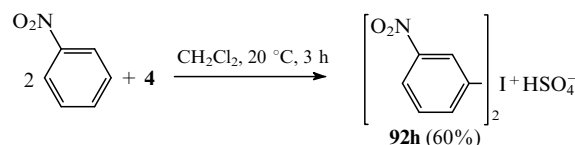
The participation of iodine fluorosulfates in aromatic electrophilic substitution has been studied only for iodosyl fluorosulfate **4**. Recently, it has been found that this compound reacts efficiently under mild conditions with benzene and its derivatives containing *ortho*- and *para*-orienting substituents to give diaryliodonium hydrogensulfates **92** with a *para*-substituted aromatic ring.¹²³



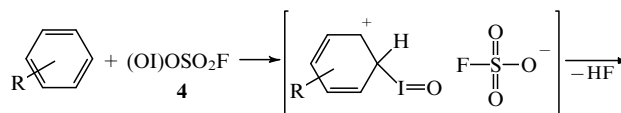
R = H: X = H (**a**), Me (**b**), Bu^t (**c**), F (**d**), Cl (**e**), Br (**f**);

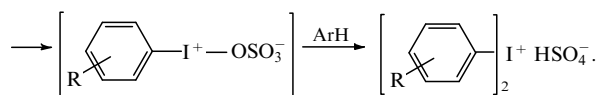
R = X = Me (**g**).

The fact that this reaction is regioselective confirms the ionic structure and, hence, the high electrophilicity of iodosyl fluorosulfate. Moreover, this compound is highly reactive towards deactivated substrates such as halobenzenes and nitrobenzene. The latter reaction occurs at room temperature and yields 3,3'-bis(nitrophenyl)iodonium salt **92h** as the only product.

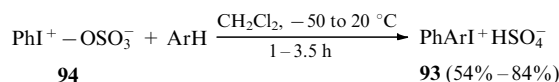


In all cases, iodonium hydrogensulfates were isolated instead of the expected fluorosulfates. This can be due to the intermediate formation of arylidonium sulfates.





The formation of iodonium hydrogensulfates **93** in the reaction of phenyliodonium sulfate **94**, generated from iodosyl benzene and sulfur trioxide,¹²⁴ with aromatic compounds¹²⁰ can serve as experimental evidence supporting this mechanism.

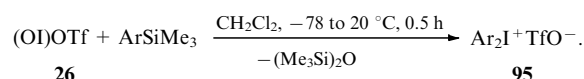


Ar = Ph, 4-MeC₆H₄, 4-FC₆H₄, 4-IC₆H₄, 4-Bu^tC₆H₄,
2,4-Me₂C₆H₃, 2,4,6-Me₃C₆H₂, 3-NO₂C₆H₄.

Unlike the above reactions involving sulfates and hydrogensulfates, which occur in sulfuric acid as a solvent and give products in low yields, the reactions with iodosyl fluorosulfate proceed under mild conditions even with aromatic compounds deactivated with respect to electrophilic attack, for example, with fluorobenzene and nitrobenzene. Since this procedure readily gives diaryliodonium salts in high yields directly from aromatic compounds, and the target products can be easily isolated, this method can find wide use in organic synthesis.

An important feature of the reactions of iodosyl fluorosulfate **4** is that they enable the preparation of diaryliodonium hydrogensulfates, which are convenient synthons that can be further converted into other iodonium salts with non-nucleophilic anions (BF₄⁻, SbF₆⁻ or PF₆⁻). In recent years, these salts have been finding increasing application as catalysts of radiation-induced cationic polymerisation.¹²⁵ In order to prepare these salts, the diaryliodonium hydrogensulfates were treated, without isolation, with aqueous solutions of inorganic salts containing the anions listed above. Thus, diaryliodonium salts with the desired non-nucleophilic anions can be obtained in one stage.^{88, 120}

It may be expected that not only iodosyl sulfates, hydrogensulfates and fluorosulfates, but also other sulfonates of polyvalent iodine would be highly reactive towards aromatic compounds. In fact, recently it has been found that iodosyl triflate **26** is a convenient reagent for the synthesis of diaryliodonium triflate **95** from trimethylsilylarenes.¹²⁶

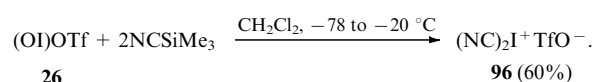


The versatility of this method was demonstrated for a wide range of alkyl- and halogen-substituted benzene derivatives. The yields of products reached 57%–93%.

It should be noted that no information about the reactions of other iodine sulfonates with aromatic compounds can be found in the literature.

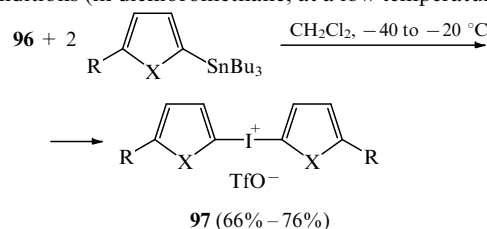
4. The reactions of iodosyl triflate with trimethylsilyl cyanide and trimethylsilylacetylenes

Apart from aromatic electrophilic substitution typical of all iodosyl sulfonates, the interaction of iodosyl triflate **26** with trimethylsilyl cyanide is also of particular interest.¹²⁷ This reaction gives rise to bis(cyano)iodonium triflate **96**.¹²⁷



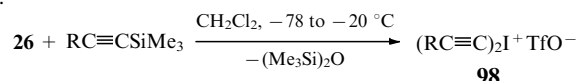
Crystalline bis-cyanide **96** is unstable. At room temperature, it entirely decomposes over a period of 3–5 min. Nevertheless, despite its instability, the bis-cyanide **96** obtained *in situ* is efficiently used in the synthesis of diaryl- and bis(hetaryl)-iodonium salts.¹²⁸ Bis(hetaryl)iodonium triflates **97** were prepared for

the first time in this way, the reaction being carried out under mild conditions (in dichloromethane, at a low temperature).¹²⁸



X = O, S; R = H, Br.

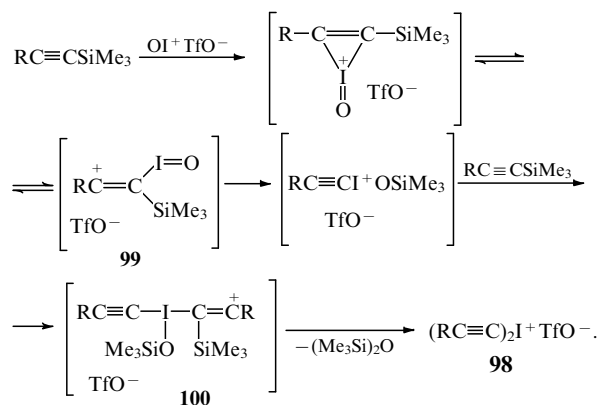
A similar reaction of iodosyl triflate **26** with trimethylsilylacetylenes results in the formation of bis(alkynyl)iodonium salts **98**.¹²⁹



R = Bu^t, Me₃Si, PrⁱSi.

The stability of the iodonium salts **98** was found to decrease in the following series of substituents: PrⁱSi > Me₃Si > Bu^t.

It can be seen from the presented examples that the synthetic strategy based on the use of iodosyl triflate is determined by its ability to react under extremely mild conditions with organic substrates containing readily leaving trimethylsilyl groups to give a highly reactive iodonium intermediate (for example, salt **100**), which subsequently decomposes with evolution of (Me₃Si)₂O.



This mechanism is supported by the fact that the vinyl cations **99** are stabilised by bulky substituents with positive inductive effects.¹²⁹

In conclusion, it should be noted that iodosyl triflate still remains the only reagent used for the synthesis of bis(cyano)- and bis(alkynyl)-iodonium salts.

V. Conclusion

The published data indicate that methods for the synthesis, the physical properties and mutual transformations of inorganic sulfonates of polyvalent iodine have been studied much more thoroughly than their reactions with organic substrates; this is confirmed by the number of relevant publications. There are only few studies devoted to electrophilic addition reactions involving certain iodine fluorosulfates and to electrophilic substitution for iodosyl sulfonates. Publications dealing with the electrophilic addition of sulfates and triflates of polyvalent iodine to alkenes are totally missing.

Nevertheless, the existing material indicates that these compounds possess unique reactivity, which permits them to be regarded as promising reagents in organic synthesis.

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New empirical models of radical abstraction reactions

E T Denisov

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Abstract. Two physical models of radical abstraction reactions are described: the model of intersecting parabolas and the model of intersecting Morse curves. A systematic account is given of the results of the analysis of a large set of experimental data (rate constants and activation energies) for a wide variety of radical reactions. It is shown that the activation energies for such reactions depend on their enthalpies, on the force constants of the reacting bonds, the strength, length, and polarity of the X–Y bond in the $X^\bullet + HY$ reaction, and also the presence in the reactants of one or several polar groups, π -bonds, and bulky groups adjoining the reaction centre. Solvation plays an important role in processes involving polar reactants. Both methods are compared as instruments for the calculation of the activation energy and bond strengths. The limits of applicability of the methods are examined. The bibliography includes 93 references.

I. Introduction

Bimolecular radical abstraction reactions are a component of the most varied chemical processes such as combustion, halogenation, the cracking and oxidation of hydrocarbons, polymerisation and degradation of polymers, photolysis and radiolysis of organic compounds, etc. They began to be investigated vigorously as early as the 1920s.

The comparison, analysis, and generalisation of data on the reactivities of molecules and radicals in various radical reactions occupy an important place in studies on bimolecular radical abstraction reactions. The first important step in this direction

was taken almost 60 years ago when Evans and Polanyi¹ established empirically the linear relation between the changes in the activation energy ΔE and the heat of reaction Δq in a series of reactions of atomic sodium with alkyl halides. Later Semenov² demonstrated in relation to extensive experimental data that the linear relation

$$E = A' + \alpha' q \quad (1)$$

holds also in other radical abstraction reactions. The Hammett³ and Taft⁴ linear correlation equations came to be widely employed in physical organic chemistry in the 1960–1970s and are also applicable to the kinetics of radical reactions.^{5,6} It has been noted in Semenov's monograph² that these correlations may be reduced to the linear equation (1). Linear correlations of this kind assist to some extent in a systematic treatment of experimental data on activation energies and rate constants, but the possibility of using them for a deep analysis of the problem of reactivity is restricted to the range of isotypical reactions. Furthermore, the treatment of the physical sense of correlation coefficients is sometimes fairly arbitrary. Quantum-chemical methods, which constitute a theoretical alternative to experimental kinetic methods, also make it possible to calculate the rate constant for a particular individual reaction.^{7–10} However, the problem of comparison and generalisation of kinetic data referring to different classes of chemical reactions as well as the problem of correlation between the reactivities of reactants and their structures and physical characteristics remain unsolved in this case too.

Several years ago, the author of the present review used a simplified model of an elementary bimolecular reaction — the intersecting parabolas model (the IP model) — in the analysis of the activation energies for a wide variety of radical abstraction reactions.^{11–13} This model can be regarded as a further development of the empirical approach initiated in the studies of Polanyi¹ and Semenov.² As a result, it became possible to separate diverse radical abstraction reactions into classes and to differentiate in each class groups of isotypical reactions. Each reaction is

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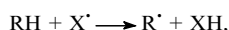
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described by two parameters referring to the entire given class of reactions: one parameter, characteristic of the group of reactions, and one individual parameter, namely the enthalpy of reaction, characteristic of the given reaction. The creation of a hierarchical system of reactions made it possible to identify at an empirical level the physical characteristics of the reactants determining the height of the activation barrier. Another model of such reactions, namely the model of two intersecting Morse potential curves (the MPC model) has been devised recently.¹⁴ The present review is devoted to the description and comparison of the results obtained by these two methods in the analysis of a large set of experimental data referring to radical abstraction reactions in the gas^{15–19} and liquid^{5,20–26} phases.

II. The intersecting parabolas model

In the IP model,^{11–13} the radical abstraction reaction



in which a hydrogen atom is transferred from the initial (RH) to the final (XH) molecule, is regarded as the result of the intersection of two potential curves, one of which describes the potential energy $U_i(r)$ of the vibration of the H atom along the bond being dissociated in the initial molecule and the other describes the potential energy $U_f(r)$ of the vibration of the same atom along the bond being formed in the reaction product (U is the potential energy and r the amplitude of the atomic vibrations along the valence bond). The stretching vibrations of the H atom in RH and XH are regarded as harmonic and are described by the parabolic law

$$U(r)^{1/2} = br.$$

The following parameters are used to characterise the elementary step in the IP model (Fig. 1).

1. The enthalpy of reaction ΔH_e which includes the difference between the zero-point energies of the broken and generated bonds:

$$\Delta H_e = D_i - D_f + 0.5hL(v_i - v_f), \quad (2)$$

where D_i and D_f are the dissociation energies of the broken (i) and generated (f) bonds, v_i and v_f are the stretching vibration frequencies of these bonds, h is the Planck constant, and L is the Avogadro number.

2. The activation energy E_e , which is linked to the experimentally determined Arrhenius energy E by the relation

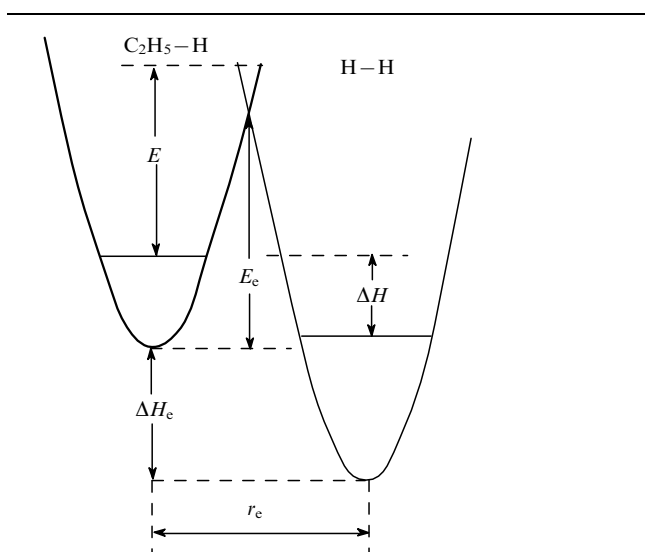


Figure 1. The energy profile of the $\text{H}^{\bullet} + \text{C}_2\text{H}_6$ reaction in the IP model.¹²

$$E_e = E + 0.5(hLv_i - RT). \quad (3)$$

3. The coefficients b_i and b_f , which describe the dependence of the potential energy on the atomic vibration amplitude along the initial (i) and final (f) valence bonds. There is a parabolic relation between the potential energy and the vibration amplitude:

$$U_i = b_i^2 r^2 \quad \text{and} \quad U_f = b_f^2 (r_e - r)^2$$

(Fig. 1). The quantity $2b^2$ is the force constant of the corresponding bond with $b = \pi v(2\mu)^{1/2}$, where μ is the reduced mass of the atoms forming the bond.

4. The distance r_e , which characterises the displacement of the abstracted atom in the elementary step.

In the IP model, these parameters are linked by the relation

$$br_e = \alpha(E_e - \Delta H_e)^{1/2} + E_e^{1/2}, \quad (4)$$

where $b = b_i$, *i.e.* refers to the attacked bonds in the molecule, while the coefficient $\alpha = b_i/b_f$ represents the ratio of the force constants of the ruptured and generated bonds raised to the power 1/2.

In the case of structurally isotypical reactions ($br_e = \text{const}$), a thermally neutral reaction ($\Delta H_e = 0$) proceeds with an activation energy E_{e0} , which is determined by two parameters, namely α and br_e (or r_e , b_i , and b_f):

$$E_{e0} = \left(\frac{br_e}{1 + \alpha} \right)^2 = \left(\frac{b_i b_f r_e}{b_i + b_f} \right)^2. \quad (5)$$

On substituting the parameter br_e in Eqn (4) by its value from Eqn (5), we obtain

$$(1 + \alpha)E_e^{1/2} = \alpha(E_e - \Delta H_e)^{1/2} + E_e^{1/2}. \quad (6)$$

Comparison of Eqns (5) and (6) makes it possible to understand the kinetic significance of the parameter br_e : it is directly proportional to the activation energy for a thermally neutral reaction raised to the power 1/2. The transition state in the IP model is characterised by the distance $r^{\ddagger}$, which is linked to the other parameters by the relation

$$\frac{r^{\ddagger}}{r_e} = \frac{E_e^{1/2}}{br_e} = \left[1 + \alpha \left(1 - \frac{\Delta H_e}{E_e} \right)^{1/2} \right]^{-1}. \quad (7)$$

In the case of a thermally neutral reaction with $\alpha = 1$, *i.e.* when the force constants of the attacked and generated bonds are equal, $r^{\ddagger}$ is equal to half the segment r_e . In the general case,

$$\left(\frac{r^{\ddagger}}{r_e} \right)_0 = \frac{1}{1 + \alpha}.$$

The parabolic model is in essence empirical, since the parameter α is calculated from spectroscopic (v_i and v_f) and atomic (μ_i and μ_f) data, while the parameter br_e (or E_{e0}) is found from the experimental activation energies E [Eqns (3) and (4)] or *via* the rate constant k by means of the Arrhenius equation

$$E = RT \ln \frac{A}{k},$$

where A is the pre-exponential factor typical for such reactions. The enthalpy of such reaction is calculated by Eqn (2) from the experimental bond dissociation energies. The calculations²⁷ showed that $br_e = \text{const}$ for structurally similar reactions. Thus $br_e = 14.74 \pm 0.21 \text{ kJ}^{0.5} \text{ mol}^{-0.5}$ for 27 reactions of peroxy radicals with the C–H bonds of aromatic alkyl-substituted hydrocarbons, which corresponds to $E_{e0} = 66.32 \pm 0.94 \text{ kJ mol}^{-1}$.²⁸

III. The intersecting Morse curves model

The model of the radical abstraction reaction based on the intersection of two Morse curves has been proposed¹⁴ to test the reliability of the results obtained with the aid of the IP model. As

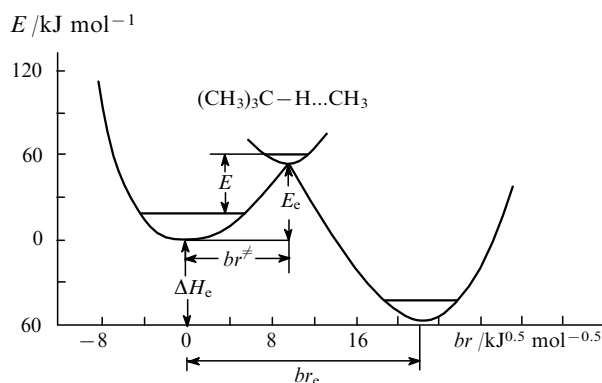


Figure 2. The energy profile of the $\text{CH}_3^\bullet + (\text{CH}_3)_3\text{CH}$ reaction in the MPC model.¹⁴

in the intersecting parabolas model, the abstraction reaction reduces in this instance to the transition of a H atom from the initial to the final state (from RH to XH), the point of intersection of two unperturbed potential curves for R–H and X–H bonds corresponding to this process (Fig. 2). However, in contrast to the IP model, in this model the atomic vibrations along valence bonds are regarded as anharmonic and are described by the corresponding Morse formula²⁹

$$U(r) = D_e [1 - \exp(-ar)]^2, \quad (8)$$

where $U(r)$ is the potential energy of the reacting bond as a function of the amplitude r of the atomic stretching vibrations along this bond, D_e is the bond dissociation energy including its zero-point vibration energy $0.5hLv$, and a is a coefficient calculated by the formula $a = bD_e^{1/2}$, in which $b = \pi v(2\mu)^{1/2}$. The elementary step in the abstraction of an atom is described by the parameters D_{ei} and D_{ef} as well as the quantities E_e , b_i , b_f ($\alpha = b_i/b_f$), and r_e , as in the parabolic model [see Eqns (2) and (3)]. The parameter br_e ($b = b_i$) is linked to the other parameters by the relation

$$br_e = -D_{ei}^{1/2} \ln \left[1 - \left(\frac{E_e}{D_{ei}} \right)^{1/2} \right] - \alpha D_{ef}^{1/2} \ln \left[1 - \left(\frac{E_e}{D_{ef}} - \frac{\Delta H_e}{D_{ef}} \right)^{1/2} \right]. \quad (9)$$

The activation energy for a thermally neutral reaction is described by the equation

$$E_{e0} = D_{ei} \left\{ 1 - \exp \left[- \frac{br_e}{D_{ei}^{1/2} (1 + \alpha)} \right] \right\}^2. \quad (10)$$

Hence it is easy to obtain an expression which elucidates the physical significance of the parameter br_e :

$$br_e = -(1 + \alpha) D_{ei}^{1/2} \ln \left[1 - \left(\frac{E_{e0}}{D_{ei}} \right)^{1/2} \right].$$

The position of the transition state, corresponding to the point of intersection of two curves (Fig. 2), is characterised by the relation

$$\frac{r_e}{r^\ddagger} = 1 + \alpha \left(\frac{D_{ei}}{D_{ef}} \right)^{1/2} \frac{\ln(1 - \Delta H_e/D_{ef})}{\ln(1 - E_e/D_{ei})}. \quad (11)$$

As in the parabolic model, the parameter br_e is calculated by Eqn (9) from experimental data (α , D_{ei} , D_{ef} , E). In the case of structurally isotypical reactions, $br_e = \text{const}$. Thus $br_e = 19.35 \pm 0.48 \text{ kJ}^{0.5} \text{ mol}^{-0.5}$ for 10 RH + H[•] reactions investigated in the gas phase.¹⁴

IV. Comparison of empirical and correlation equations

The IP model can be regarded as a special case of the MPC model if one is dealing with reactions having low activation energies whereupon $E_e/D_{ei} \ll 1$ and $E_e/D_{ef} \ll 1$. On expanding the logarithmic function in Eqn (9) in Maclaurin's series [$\ln(1-x) \approx x - 0.5x^2 + \dots$] and retaining only one term, we pass in this case from Eqn (9) to Eqn (4).

In order to compare Eqn (4) for the parabolic model with the Polanyi–Semenov equation [Eqn (1)],^{1,2} it is useful to transform Eqn (4) by expressing E_e explicitly as a function of ΔH_e , α , and br_e . For not unduly high values of ΔH_e , whereupon

$$\Delta H_e \ll \frac{(br_e)^2}{1 - \alpha^2}, \quad (12)$$

we obtain the expression

$$E_e = \left(\frac{br_e}{1 + \alpha} + \frac{\alpha \Delta H_e}{2br_e} \right)^2. \quad (13)$$

Since α' in the Polanyi–Semenov equation represents the ratio $\Delta E/\Delta \Delta H$, it follows that, after substituting Eqn (13) in Eqn (1), we obtain

$$\alpha' = \frac{\Delta E_e}{\Delta H_{e2} - \Delta H_{e1}} = \frac{\alpha}{(1 + \alpha)} + \frac{0.25\alpha^2}{(br_e)^2} (\Delta H_{e2} + \Delta H_{e1}), \quad (14)$$

where H_{e2} and H_{e1} are respectively the maximum and minimum enthalpies in the series of reactions considered. Analysis of the second term shows that the empirical coefficient α' depends not only on the force constants of the reacting bonds ($\alpha = b_i/b_f$) but also on the range of variation of the enthalpies in the given series of reactions. This is natural, since the dependence of E on ΔH is nonlinear. For a sufficiently wide range of variation of ΔH , whereupon condition (12) does not hold, the dependence of α' on the parameters α , br_e , and ΔH_e becomes more complex and is expressed by the following formula obtained from Eqn (4):

$$\alpha' = \frac{\alpha^2}{1 - \alpha^2} + \frac{2\alpha}{(1 - \alpha^2)^2} f(br_e, \Delta H_e), \quad (15)$$

where

$$f(br_e, \Delta H_e) = \frac{(br_e)^2}{\Delta H_{e2} - \Delta H_{e1}} \left\{ \left[1 - \frac{\Delta H_{e1}(1 - \alpha^2)}{(br_e)^2} \right]^{1/2} - \left[1 - \frac{\Delta H_{e2}(1 - \alpha^2)}{(br_e)^2} \right]^{1/2} \right\}.$$

It is seen from Eqns (14) and (15) that the coefficient α' in Eqn (1) depends not only on the physical parameters (b_i , b_f , and r_e) but also on an incidental factor such as the range of variation of the enthalpies in the selected series of reactions. By virtue of this factor, the parameter α' in Eqn (1) can characterise only approximately the physical factors influencing the activation energy and this characterisation is less accurate the wider the range of variation of the enthalpies. This in fact explains, in particular, the experimentally observed parallel variation of α' and A' in the $\text{X}^\bullet + \text{RH}$ reactions³⁰ [see Eqns (14) and (15)]:

$\text{X}^\bullet$	$\text{HO}^\bullet$	$\text{H}^\bullet$	$\text{O}^\bullet$	$\text{CH}_3^\bullet$	$\text{CCl}_3^\bullet$
α'	0.25	0.38	0.52	0.52	0.94
$A' / \text{kJ mol}^{-1}$	31	46	64	62	67

The above considerations, concerning the Polanyi–Semenov method, refer also to the empirical procedure for the estimation of

activation energy proposed by Szabo.³¹ According to the latter, the activation energy for a radical reaction can be determined from the following simple formula:

$$E = D_i - \alpha' D_f.$$

Since $\Delta H = D_i - D_f$ and the activation energy $E = E_0 = D_i(1 - \alpha')$ when $\Delta H = 0$, it follows that $E = E_0 + \alpha' \Delta H$ and the coefficient α' is expressed by Eqn (14) within the framework of the parabolic model.

The correlations between the rate constants for a wide variety of reactions are widely used in the scientific literature:

$$\lg \frac{k}{k_1} = \rho \sigma, \quad (16)$$

where σ is the Hammett,³ Taft,⁴ *etc.* function and ρ is an empirical coefficient. Together with Eqn (1), this equation is frequently applied to radical abstraction reactions.⁶ Since the pre-exponential factor calculated per one reacting bond is constant for each series of radical reactions²⁸ and

$$\Delta E = -2.3RT \lg \frac{k}{k_1},$$

the following expression arises from Eqn (13):

$$\rho = \frac{\alpha T_0}{(1 + \alpha)T} \frac{\Delta \Delta H_e}{\Delta \Delta G_0} + \frac{\alpha^2 T_0}{4(br_e)^2 T} \frac{\Delta \Delta H_e^2}{\Delta \Delta G_0}. \quad (17)$$

Here the difference between the free energies $\Delta \Delta G_0$ concerns the reference reactions on which the comparison is based. It is linked to σ by the simple relation $\Delta \Delta G_0 = -2.3RT_0 \sigma$. As can be seen from Eqn (17), the coefficient ρ depends not only on the parameters of the reactants (α , br_e) and temperature (T_0/T), but also on the range of variation of ΔG_0 and ΔH_e . This naturally hinders its use for the identification of the physical factors determining the reactivity of the reactants. The expression for ρ becomes still more cumbersome if the series includes reactions characterised by different coefficients br_e . However, despite this, a relation of type (17) frequently reduces to an equation of type (1) in the kinetics of radical reactions, which has been noted in Semenov's monograph.²

A fairly simple empirical equation, relating the activation energies for the forward (E) and reverse ($E + \Delta H$) bimolecular reactions, has been proposed:³²

$$E(E + \Delta H) = \varepsilon^2. \quad (18)$$

By transforming Eqn (13), we obtain the following expression, within the framework of the parabolic model, for the activation energies for the forward (E_e) and reverse (E'_e) reactions (for the reverse reaction, $b' = b/\alpha$, $\alpha' = \alpha^{-1}$, and $\Delta H'_e = -\Delta H_e$):

$$(E_e E'_e)^{1/2} = \left(\frac{br_e}{1 + \alpha} \right)^2 + \frac{\Delta H_e(\alpha - 1)}{2(\alpha + 1)} - \frac{\alpha \Delta H_e^2}{4(br_e)^2}. \quad (19)$$

It is seen from the comparison of Eqns (18) and (19) that the product $E_e E'_e$ does indeed tend to a constant value with decrease in ΔH_e and $\varepsilon^{1/2} = br_e/(1 + \alpha)$.

The parabolic model of radical reactions¹² is close to the Marcus model for the transfer of an electron and a proton,³³ but differs from it by two significant features. In the IP model, one considers the involvement in the elementary step of the individual R–H and X–H bonds, each of which is characterised by an intrinsic force constant (the coefficients b_i and b_f). Furthermore, account is taken of the zero-point vibration of the bond as its inherent characteristic.

The reduction of the reaction in the IP and MPC models to the migration of the attacked atom determined by the intersection of unperturbed potential curves is an evident simplification. In fact the orbitals are perturbed in the RH + H[•] reactions and the electron densities of the orbitals of the R–H and X–H bonds overlap, which is a topic considered in quantum chemistry.^{7–10}

The question arises how the results of quantum-chemical calculations and the empirical parameter r_e , calculated with the aid of the IP and MPC models, are related. The most accurate quantum-chemical calculation of the energy profile of the abstraction reaction has been carried out for the H[•] + H₂ reaction.⁹ According to this calculation, the height of the potential barrier is 41 kJ mol^{−1}.³⁴ The following values of E_e and r_e correspond to this value of E in the IP and MPC models: $E_e = 66.1$ kJ mol^{−1} at $T = 300$ K [see Eqn (3)], $r_e = 3.67 \times 10^{-11}$ m (MPC model), and $r_e = 3.10 \times 10^{-11}$ m (IP model). The width of the potential barrier at the level of half its height is 9.6×10^{-11} m according to the quantum-chemical calculation.³⁴ Thus the distance r_e amounts to 32% of half the width of the potential barrier in the IP model and to 38% in the MPC model.

V. Classification of radical abstraction reactions

The two models of the radical abstraction reactions (IP and MPC) have an evident similarity: they take into account the relation between the activation energy and physical characteristics of the reacting bonds such as the dissociation energy and the force constant. The bond dissociation energy is an individual characteristic of the molecule entering into the reaction or formed. The force constants for the stretching vibration of bonds ($2\pi^2\nu^2\mu$) of each type (C–H, O–H, *etc.*) are virtually identical for the entire class of isotypical compounds. This important factor makes it possible to classify radical abstraction reactions in terms of the type of reacting bonds and the coefficients b characterising them. A pair of coefficients — b_i and b_f or $b = b_i$ and $\alpha = b_i/b_f$ — corresponds to each class of such reactions. In the calculation of the activation energy E_e from E and conversely, the zero-point vibration energy of the ruptured bond also becomes important [see Eqn (3)]. The quantities α , b , and $0.5hLv_i$ for the radical abstraction reactions of compounds in different classes are listed in Table 1.

Knowing these parameters, it is easy to find the analogous characteristics of the reverse reactions. For a reverse reaction, to which the index f corresponds, we have $\alpha_f = \alpha^{-1}$, $b_f = b/\alpha$, and $0.5hLv_f = 0.5hLv_i/\alpha$. For example, $\alpha_f = 0.796^{-1} = 1.256$, $b_f = (3.743 \times 10^{11})/\alpha = 4.702 \times 10^{11}$ kJ^{0.5} mol^{0.5} m^{−1}, and $0.5hLv_f = 17.4/0.796 = 21.8$ kJ mol^{−1} for the R[•] + HOR reaction.

The class of radical abstraction reactions may include a single reaction (for example, H[•] + HCl), one group of reactions (for example, R[•] + NH₃, where R[•] is any alkyl radical), or several such groups (for example, the class of reactions RO₂[•] + R'H, where R'H is a hydrocarbon, consists of three groups of reactions: RO₂[•] + R¹H, RO₂[•] + R²H, and RO₂[•] + R³H, where R¹H, R²H, and R³H are any aliphatic, unsaturated, and aromatic alkyl-substituted hydrocarbons respectively). All the reactions belonging to one group are characterised by a single parameter r_e or br_e . Table 2 presents the results of the calculation of the parameters br_e by Eqns (4) (the IP model)³⁵ and (9) (the MPC model)¹⁴ for reactions of the class H[•] + RH. The quantities br_e calculated on the basis of one model for reactions involving hydrocarbons having different structures are very close; the average values of br_e are 15.30 ± 0.59 kJ^{0.5} mol^{−0.5} in the IP model and $19.42 + 0.98$ kJ^{0.5} mol^{−0.5} in the MPC model. The activation energies were calculated by the Arrhenius equation; the quantity A calculated per reacting C–H bond is 10^9 litre mol^{−1} s^{−1} for the liquid phase and 2×10^8 litre mol^{−1} s^{−1} for the gas phase. Knowing the parameter br_e , it is possible to calculate an important characteristic of the reactivity of each group of reactions such as the activation energy for a thermally neutral reaction E_{e0} [Eqns (5) and (10)]. The energies E_{e0} may differ significantly for reactions of different classes. Thus the following values have been obtained (kJ mol^{−1}) for reactions involving aliphatic hydrocarbons R¹H:

Reaction	H [•] + R ¹ H	R [•] + R ¹ H	RO ₂ [•] + R ¹ H
E_{e0} (IP) ^{27,36}	64.8	68.2	58.1
E_{e0} (MPC) ¹⁴	66.1	71.3	61.8

Table 1. Kinetic parameters of radical abstraction reactions of different classes.²⁷

Reaction	α	$10^{-11}b$ /kJ ^{0.5} mol ^{-0.5} m ⁻¹	$0.5hLv_i$ /kJ mol ⁻¹	$0.5hL(v_i - v_f)$ /kJ mol ⁻¹	$(r^\ddagger/r_e)_0$
H [•] + H ₂	1.000	4.133	26.3	0.0	0.500
H [•] + HCl	0.953	3.937	17.9	-8.4	0.488
H [•] + HBr	0.851	3.516	15.2	-11.1	0.460
H [•] + HI	0.743	3.072	13.8	-12.5	0.426
H [•] + RH	0.906	3.743	17.4	-8.9	0.475
H [•] + NH ₃	1.042	4.306	20.0	-6.3	0.510
H [•] + HOCH ₃	1.137	4.701	21.7	-4.6	0.532
H [•] + HSiR ₃	0.668	2.756	12.6	-13.6	0.400
H [•] + H ₂ S	0.831	3.434	15.6	-10.7	0.454
H [•] O + CH ₄	0.790	3.743	17.4	-4.4	0.441
H [•] O + NH ₃	0.908	4.306	20.0	-1.8	0.472
H [•] O + HOCH ₃	0.992	4.701	21.7	-0.1	0.498
H [•] O + SiH ₄	0.591	2.861	13.1	-8.7	0.372
H [•] O + HS ₂	0.724	3.434	15.6	-6.2	0.420
R [•] + R'H	1.00	3.743	17.4	0.0	0.500
R [•] + H ₂ NR'	1.207	4.517	20.9	3.5	0.547
R [•] + HSiR' ₃	0.723	2.756	12.6	-4.8	0.420
R [•] + HSR'	0.808	3.026	13.8	-3.6	0.447
RO [•] + R'H	0.796	3.743	17.4	-4.3	0.443
RO [•] + HSiR' ₃	0.581	2.756	12.6	-9.1	0.367
RO ₂ [•] + R'H	0.814	3.743	17.4	-3.8	0.449
RO ₂ [•] + HOOR'	1.000	4.600	21.2	0.0	0.500
RO ₂ [•] + HOAr	1.000	4.665	21.5	0.3	0.500
RO ₂ [•] + HOAm	1.000	4.665	21.5	0.3	0.500
RO ₂ [•] + HAm	0.940	4.324	20.0	-1.2	0.484
RO ₂ [•] + HSAr	0.658	3.026	13.8	-7.4	0.397
ArO [•] + HR	0.802	3.743	17.4	-4.1	0.445
ArO [•] + HOAr'	1.000	4.665	21.5	0.0	0.500
ArO [•] + HOAm	1.000	4.665	21.5	0.0	0.500
ArO [•] + HAm	0.927	4.324	20.0	-1.5	0.481
Am [•] + HAm	1.000	4.324	20.0	0.0	0.500
Am [•] + HOAm	1.079	4.665	21.5	1.5	0.519
AmO [•] + HOAr	1.000	4.665	21.5	0.0	0.500
AmO [•] + HAm	0.927	4.324	20.0	-1.5	0.481
AmO [•] + HOAm	1.000	4.665	21.5	0.0	0.500
AmO [•] + HR	0.802	3.743	17.4	-4.1	0.445
AmO [•] + HSAr	0.649	3.026	13.8	-7.7	0.394
R ₃ Si [•] + HSiR'	1.000	2.752	12.6	-8.9	0.500

^a Here and henceforth AmH = amine, AmOH = hydroxylamine, Am[•] = aminyl radical, and AmO[•] = nitroxyl radical.

For reactions of one class, the values of E_{e0} found on the basis of both models are very close, the discrepancy not exceeding 3 kJ mol⁻¹.

The classification of radical reactions carried out in this way makes it possible to observe empirically (on the basis of the parameter br_e) structural differences between reactants within one class, to compare the classes and groups of reactions in terms of reactivity (in terms of the parameter br_e or E_{e0}), and to identify the physical factors determining the reactivities of groups of reactants. The parameters br_e for different groups of reactions are presented in Table 3.

The reactions of nitrogen- and oxygen-centred radicals with O–H and N–H bonds take place in solution in two stages *via* the preliminary formation of a hydrogen-bonded complex, for example:



The observed rate constant is the product of the equilibrium constant for the first stage and the rate constant for the second stage. However, in the gas phase such reactions apparently proceed as bimolecular processes. Therefore, in order to compare

the parameters of these reactions in the gas and liquid phases and for their correct comparison with other bimolecular reactions, they were all regarded as bimolecular and the experimental pre-exponential factors were used in the calculations.

The activation energy for any individual reaction within the limits of the given group of reactions may be calculated correctly from the parameter br_e . Within the framework of the IP model, the quantity E_e was calculated by means of the following formulae:²⁷

(1) for $\alpha = 1$,

$$E_e^{1/2} = 0.5br_e + \frac{\Delta H_e}{2br_e}; \quad (20)$$

(2) for $\alpha \neq 1$

$$E_e^{1/2} = \frac{br_e}{1 - \alpha^2} \left\{ 1 - \alpha \left[1 - \frac{1 - \alpha^2}{(br_e)^2} \Delta H_e \right]^{1/2} \right\}; \quad (21)$$

(3) for $\Delta H_e(1 - \alpha^2) \ll (br_e)^2$

$$E_e^{1/2} = \frac{br_e}{1 + \alpha} + \frac{\alpha \Delta H_e}{2br_e}. \quad (22)$$

Table 2. Kinetic characteristics of the $H^+ + RH$ reactions calculated with the aid of the IP³⁵ and MPC¹⁴ models.

RH	Medium	T/K	$k/\text{litre mol}^{-1} \text{ s}^{-1}$	$-\Delta H_e/\text{kJ mol}^{-1}$	$E_{ei}/\text{kJ mol}^{-1}$	$br_e/\text{kJ}^{0.5} \text{ mol}^{-0.5}$	
						IP	MPC
CH ₄	Gas	298	2.24×10^2	6.5	64.9	15.71	19.83
CH ₃ CH ₃	"	298	2.42×10^4	26.5	54.4	15.52	19.63
CH ₃ CH ₂ CH ₃	"	298	5.84×10^3	27.3	55.1	15.65	19.84
CH ₃ CH ₂ CH ₃	"	416	1.88×10^7	42.4	42.2	14.83	18.67
CH ₃ (CH ₂) ₂ CH ₃	"	512	2.60×10^6	27.3	49.4	14.96	18.74
CH ₃ (CH ₂) ₂ CH ₃	"	298	3.56×10^4	41.6	49.0	15.62	19.93
CH ₃ (CH ₂) ₃ CH ₃ ^a	"	763	1.02×10^8	41.6	47.8	15.48	19.68
CH ₃ (CH ₂) ₃ CH ₃ ^a	"	763	1.20×10^9	41.6	43.4	14.94	18.84
CH ₃ (CH ₂) ₃ CH ₃ ^a	"	763	1.37×10^8	41.6	52.8	15.37	19.40
Pr ⁱ CH ₂ CH ₃	"	673	6.76×10^7	41.6	50.3	15.78	18.92
CH ₃ (CH ₂) ₄ CH ₃	RH	313	6.10×10^4	41.6	47.7	15.47	19.67
Bu ⁱ CH ₂ CH ₃	RH	296	2.30×10^4	41.6	53.8	16.18	20.86
Me ₂ CHCHMe ₂	RH	313	4.80×10^6	52.7	42.0	15.30	19.52
CH ₃ CH(CH ₂ CH ₃) ₂	RH	296	8.30×10^6	52.7	48.9	16.12	20.88
Pr ⁱ ₂ CH ₂	RH	296	2.60×10^5	52.7	47.9	16.00	20.68
CH ₃ (CH ₂) ₁₀ CH ₃	RH	313	5.00×10^6	41.6	47.9	15.49	19.71
cyclo-C ₅ H ₁₀	H ₂ O	288	3.00×10^7	49.5	41.2	15.05	19.08
cyclo-C ₆ H ₁₂	H ₂ O	288	3.00×10^7	45.3	41.6	14.90	18.80
cyclo-C ₆ H ₁₂	RH	313	3.20×10^6	45.3	47.7	15.64	20.00
cyclo-C ₆ H ₁₁ (CH ₃)	RH	396	1.40×10^5	56.4	47.6	16.14	20.94

^a The quantities k , E_{ei} and br_e have been taken from different sources.

Table 3. The pre-exponential factors A (calculated for one reacting bond), the parameters br_e , and the quantities $\Delta H_{e, \min}$ and $\Delta H_{e, \max}$ for different groups of radical reactions in terms of the IP model.

Reaction	$10^{-8} A/\text{litre mol}^{-1} \text{ s}^{-1}$	$br_e/\text{kJ}^{0.5} \text{ mol}^{-0.5}$	$\Delta H_{e, \min}/\text{kJ mol}^{-1}$	$\Delta H_{e, \max}/\text{kJ mol}^{-1}$	Ref.
$R^{\bullet} + R^1H$	10	17.23	-153.1	153.1	27
$R^{\bullet} + R^2H$	1.0	18.86	-198.4	198.4	27
$R^{\bullet} + R^3H$	1.0	18.11	-176.9	176.9	27
$R^{\bullet} + R'_3SiH$	10	13.18	-147.3	100.0	37
$RO^{\bullet} + R^1H$	10	13.37	-99.7	83.6	27
$RO^{\bullet} + R^2H$	1.0	14.41	-131.6	105.6	27
$RO^{\bullet} + R^3H$	1.0	14.16	-123.6	100.1	27
$RO^{\bullet} + R'_3SiH$	10	10.13	-82.6	52.5	37
$RO_2^{\bullet} + R^1H$	0.1	14.23	-120.5	88.1	28
$RO_2^{\bullet} + R^2H$	0.1	15.68	-167.7	120.6	28
$RO_2^{\bullet} + R^3H$	0.1	14.74	-136.4	99.1	28
$RO_2^{\bullet} + ROOH$	10	13.13	-51.5	51.5	27
$RO_2^{\bullet} + Ar^1OH$	0.32	13.46	-56.3	56.3	38
$RO_2^{\bullet} + Ar^2OH$	0.32	14.40	-73.8	73.8	38
$RO_2^{\bullet} + AmH$	1.0	12.12	-41.2	42.7	39
$RO_2^{\bullet} + ArSH$	0.32	10.39	-70.4	45.7	40
$Ar^1O^{\bullet} + R^3H$	1.0	15.53	-167.3	131.1	41
$Ar^1O^{\bullet} + HOAr^1$	10	12.61	-42.1	42.1	41
$Ar^1O^{\bullet} + AmH$	1.0	10.13	-11.2	15.8	41
$AmO^{\bullet} + AmH$	1.0	11.63	-33.5	36.0	42
$Am^{\bullet} + R^3H$	1.0	16.87	-187.5	158.4	43
$AmO^{\bullet} + HOAr^1$	1.0	12.93	-47.3	47.3	42
$R_3Si^{\bullet} + R'_3SiH$	10	13.69	-90.2	90.2	37

In the MPC model, the activation energy E_e was found by the numerical solution of the equation¹⁴

$$F(E_e) = D_{ei}^{1/2} \ln \left[1 - \left(\frac{E_e}{D_{ei}} \right)^{1/2} \right] + \alpha D_{ef}^{1/2} \ln \left[1 - \left(\frac{E_e - \Delta H_e}{D_{ef}} \right)^{1/2} \right] + br_e = 0. \quad (23)$$

The Newton–Raphson method combined with a special computer program was used to solve Eqn (23) for fixed values of D_{ei} , D_{ef} , and α . Table 4 presents the results of the calculation of the activation energies for the $H^+ + RH$ reactions based on the IP and MPC models as well as experimental values of $E_{e, \exp}$. The discrepancy between the calculated and experimental data for the IP and MPC models is 1.2 ± 0.8 and 1.0 ± 0.7 kJ mol⁻¹ respectively, *i.e.* it does not exceed the scatter of experimental activation energies (± 3 kJ mol⁻¹).

Table 4. Comparison of the experimental activation energies ($E_{\text{c,exp}}$)^{18,21} and the activation energies calculated on the basis of the IP³⁵ and MPC¹⁴ models for the $\text{H}^\bullet + \text{RH}$ reactions.

RH	Medium	T/K	$-\Delta H_{\text{e}}/\text{kJ mol}^{-1}$	$E_{\text{c,exp}}/\text{kJ mol}^{-1}$	$E_{\text{c}}/\text{kJ mol}^{-1}$	
					MPC	IP
CH_3OH	H_2O	300	49.1	44.2	43.5	42.7
CH_3OH	Gas	298	49.1	45.8	43.5	42.7
$\text{CH}_3\text{CH}_2\text{OH}$	H_2O	300	53.2	40.2	41.7	41.2
$\text{CH}_3\text{CH}_2\text{OH}$	Gas	298	53.2	40.8	41.7	41.2
$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	H_2O	298	56.7	38.3	40.1	39.9
$\text{CH}_2\text{OHCH}_2\text{OH}$	H_2O	300	54.6	41.8	41.1	40.7
$\text{CH}_2\text{OHCHOHCH}_2\text{OH}$	H_2O	300	60.6	36.8	38.5	38.5
$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$	H_2O	300	81.8	30.3	29.9	31.5
$\text{CH}_2=\text{CHCH}_2\text{OH}$	H_2O	300	103.5	21.7	21.1	24.7
$(\text{CH}_3)_2\text{CHOH}$	H_2O	300	62.7	35.3	37.6	37.7
$(\text{CH}_3\text{CH}_2)_2\text{O}$	H_2O	288	61.2	37.9	38.2	38.3
$[(\text{CH}_3)_2\text{CH}]_2\text{O}$	H_2O	313	71.5	34.1	33.8	34.6
	H_2O	300	59.0	40.0	39.1	39.0
	RH	313	59.0	38.0	39.1	39.0
	H_2O	313	59.0	41.0	39.1	39.0
$\text{CH}_3\text{CH}_2\text{COOH}$	H_2O	288	55.9	41.0	40.5	40.2
HCOOH	H_2O	300	40.7	46.9	47.2	46.0
$\text{CH}_3(\text{CH}_2)_2\text{COOH}$	H_2O	298	55.9	41.5	40.5	40.2
$\text{CH}_3(\text{CH}_2)_2\text{COOH}$	H_2O	288	55.9	40.3	40.5	40.2
$(\text{CH}_3)_2\text{CHCOOH}$	H_2O	288	66.2	36.0	36.1	36.6

VI. Dissociation energies and force constants of the attacked and generated bonds

A clear-cut dependence of the activation energy on the heat (enthalpy) of reaction, which is equal in its turn to the difference between the dissociation energies of the ruptured (D_{r}) and generated (D_{g}) bonds, has been established for radical abstraction reactions.^{2,30} In both models considered in the present review, the values of D_{ei} and D_{ef} , incorporating the zero-point energy of the bond vibrations, are examined. The enthalpy of reaction ΔH_{e} therefore also includes the difference between these energies [see Eqn (2)].

As noted above, all radical abstraction reactions can be divided into groups and the activation energy E_{e0} for a thermally neutral reaction can be calculated in each group. The possibility of calculating the activation energy for any reaction of the given series (group) from the value of E_{e0} (or br_{e}) and of estimating the contribution of the enthalpy to the activation energy follows from this important factor. The contribution of ΔE_{H} represents the difference between the activation energies for the given (i th) reaction and a thermally neutral reaction characterised by the quantity E_{e0} :²⁷

$$\Delta E_{\text{H}} = E_{\text{ei}} - E_{\text{e0}}. \quad (24)$$

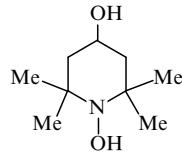
As an example, Table 5 presents the values of ΔE_{H} for the reactions of peroxy radicals with antioxidants of different classes.⁴⁴ It follows from the table that the ratio $\Delta E_{\text{H}}/\Delta H$ for these groups of reactions is close to 1/2.

In terms of the parabolic model, it is possible to obtain simple and physically clear equations for the estimation of ΔE_{H} as a function of α , br_{e} , and ΔH_{e} . The following simple expressions follow from the combination of Eqns (5) and (2)–(22):²⁷

(1) for $\alpha = 1$

$$\Delta E_{\text{H}} = 0.5\Delta H_{\text{e}} + \frac{0.25}{(br_{\text{e}})^2} \Delta H_{\text{e}}^2; \quad (25)$$

Table 5. The contributions of the enthalpy ΔE_{H} to the activation energy E for the reactions of a secondary peroxy radical with various inhibitors (ΔH , E , and ΔE_{H} in kJ mol^{-1}).⁴⁴

Inhibitor	ΔH	E	ΔE_{H}
PhOH	1.5	25.9	0.7
4-MeC ₆ H ₄ OH	−7.7	21.4	−3.8
4-MeOC ₆ H ₄ OH	−16.5	17.3	−7.9
4-PhCH ₂ C ₆ H ₄ OH	−18.0	16.6	−8.6
4-AcC ₆ H ₄ OH	4.0	27.2	2.0
2,3-Me ₂ C ₆ H ₃ OH	−12.0	19.4	−5.8
α -HOC ₁₀ H ₇	−24.1	13.9	−11.3
2,6-Bu ₂ ^t C ₆ H ₃ OH	−18.8	22.8	−8.9
2,6-Bu ₂ ^t -4-MeC ₆ H ₂ OH	−26.5	19.3	−12.4
2,6-Bu ₂ ^t -4-MeOC ₆ H ₂ OH	−34.8	15.8	−15.9
2,6-Bu ₂ ^t -4-BnC ₆ H ₂ OH	−27.8	18.8	−12.9
2,6-Bu ₂ ^t -4-PhSC ₆ H ₂ OH	−19.1	22.6	−9.1
Si[2,6-Bu ₂ ^t -4-CH ₂ CH ₂ OC ₆ H ₂ OH] ₄	−24.6	20.2	−11.5
Ph ₂ NH	−0.8	12.0	−0.4
(4-MeC ₆ H ₄) ₂ NH	−14.9	5.7	−7.8
(4-MeOC ₆ H ₄) ₂ NH	−24.3	1.8	−11.7
4-MeOC ₆ H ₄ NHPh	−18.3	4.2	−9.3
1-C ₁₀ H ₇ NHPh	−13.6	6.2	−7.3
4-PhHNC ₆ H ₄ NHPh	−18.6	4.1	−9.4
Bu ₂ ^t C = NOH	−27.0	27.1	−12.7
PhCH = CHC(O)N(OH)Bu ^t	−44.1	19.8	−20.0
	−63.3	12.4	−27.4
PhSH	−37.1	11.9	−15.0
4-MeC ₆ H ₄ SH	−30.7	13.7	−13.2

(2) for $\alpha \neq 1$,

$$(1 - \alpha^2)\Delta E_H = 2\alpha(br_e)^2 - \alpha^2\Delta H_e - 2\alpha(br_e)^2 \left[1 - \frac{(1 - \alpha^2)}{(br_e)^2} \Delta H_e \right]^{1/2}; \quad (26)$$

(3) for $\Delta H_e(1 - \alpha^2) \ll (br_e)^2$,

$$\Delta E_H = \frac{\alpha}{1 + \alpha} \Delta H_e + \frac{0.25\alpha}{(br_e)^2} \Delta H_e^2. \quad (27)$$

It is seen from Eqns (25) and (27) that, for low values of the enthalpy of reaction, ΔE_H is directly proportional to ΔH_e which agrees with the Polanyi–Semenov equation.² The slope of the linear plot of ΔE_H as a function of ΔH_e depends on α , *i.e.* on the force constants of the bonds. The ratio $\Delta E_H/E_{e0} = \alpha(1 + \alpha)^{-1}$, which includes the force constants of the reacting bonds, may serve as a parameter of the sensitivity of E_e to ΔH_e for low values of the latter. For reactions of different classes, the coefficient α varies in the range from 0.6 to 1.7 and the coefficient $\alpha(1 + \alpha)^{-1}$ therefore varies from 0.38 to 0.63.

The activation energy increases with increase in ΔH_e and diminishes with increase in $|\Delta H_e|$ for $\Delta H_e < 0$. On the other hand, according to the law of conservation of energy, $E > 0$ for exothermic reactions and $E \geq \Delta H_e$ for endothermic reactions. It follows from the law of conservation of energy and Eqns (2)–(4) that the parameter br_e for one group of reactions is constant, while ΔH_e varies in the range $\Delta H_{e,\min} \leq \Delta H_e \leq \Delta H_{e,\max}$.⁴⁵ For highly endothermic reactions with $\Delta H_e > \Delta H_{e,\max}$, the activation energy is $E = \Delta H + 0.5RT$, whilst for exothermic reactions with $\Delta H_e < \Delta H_{e,\min}$ it is $0.5RT$. The limiting enthalpies of reaction $\Delta H_{e,\max}$ and $\Delta H_{e,\min}$ are related to the parameters br_e and α in the following way:⁴⁵

$$\Delta H_{e,\max} = (br_e)^2 + 2\alpha br_e(0.5hLv_f)^{1/2} + 0.5(\alpha^2 - 1)hLv_f, \quad (28)$$

$$\Delta H_{e,\min} = -\left(\frac{br_e}{\alpha}\right)^2 + 2\alpha br_e(0.5hLv_i)^{1/2} + 0.5(1 - \alpha^2)hLv_i. \quad (29)$$

As can be seen from Eqns (28) and (29), the range of variation of ΔH_e in which $br_e = \text{const}$ is wider the greater the parameter br_e . For the reactions of alkyl radicals with aliphatic hydrocarbons ($\alpha = 1$, $br_e = 17.23 \text{ kJ}^{0.5} \text{ mol}^{-0.5}$), we have $\Delta H_{e,\max} = |\Delta H_{e,\min}| = 153.1 \text{ kJ mol}^{-1}$, *i.e.* the range of enthalpies ΔH_e where $br_e = \text{const}$ is 306 kJ mol^{-1} . The enthalpies $\Delta H_{e,\max}$ and $\Delta H_{e,\min}$ for different groups of reactions are listed in Table 3.

Yet another important characteristic of radical abstraction reactions is the force constants of the ruptured and generated bonds. The dependence of the activation energy for reactions of the type $R^\cdot + RX \rightarrow RX + R^\cdot$, where $X = \text{H, Cl, Br, or I}$, on the coefficients b_i and b_f has been demonstrated experimentally.⁴⁶ It was found that $r_e = \text{const}$ in these reactions, whilst the activation energy for a thermally neutral reaction is directly proportional to the force constant of the ruptured bond. It is seen from Fig. 3 that the smaller the force constant of the C–H bond, the lower E_{e0} and that this relation is linear. The same result has been obtained⁴⁶ also for reactions of the $H^\cdot + RCl$, $H^\cdot + RBr$, and $H^\cdot + RI$ classes. Analysis of the seven classes of reactions listed above within the framework of the MPC model⁴⁷ yielded a similar result (Fig. 3). The relation

$$E_{e0}^{1/2} = \gamma \frac{b}{1 + \alpha}, \quad (30)$$

holds in this case and the proportionality coefficient γ for reactions of the $R^\cdot + RX$ and $H^\cdot + RX$ types is very close in both models: $\gamma = (4.80 \pm 0.15) \times 10^{-11} \text{ m}$. This confirms the important role of the force constant of the reacting bonds in the formation of the activation barrier. The activation energies for the $R^\cdot + RX$ reactions can be easily estimated from the empirical formula

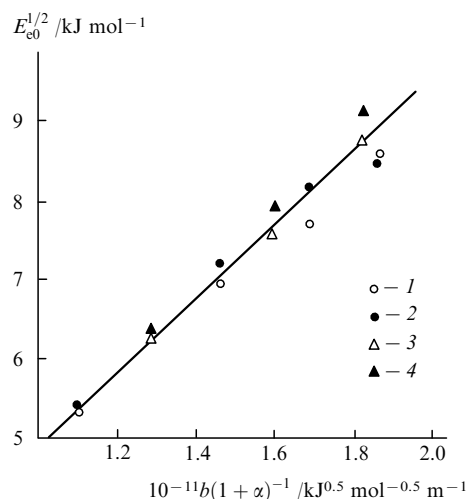


Figure 3. Dependence of E_{e0} on the coefficient $b(1 + \alpha)^{-1}$ for the $R^\cdot + RX$ ($X = \text{H, Cl, Br, I}$) reactions on the basis of the IP (1)⁴⁶ and MPC (2)⁴⁷ models and the $H^\cdot + RX$ ($X = \text{Cl, Br, I}$) reactions on the basis of the IP (3)⁴⁶ and MPC (4)⁴⁷ models.

$$E_{e0}^{1/2} = 2.31 \times 10^{-11}b + 1.08 \times 10^{10} \frac{\Delta H_e}{b}, \quad (31)$$

while those for the $H^\cdot + RX$ ($X = \text{Cl, Br, I}$) reactions can be found from the formula

$$E_e^{1/2} = 4.81 \times 10^{-11} \frac{b}{1 + \alpha} + 1.04 \times 10^{10} \alpha \frac{\Delta H_e}{b}. \quad (32)$$

VII. The role of the X–Y bond in the $X^\cdot + HY$ reaction

The hydrogen atom migrates from Y to X in the $X^\cdot + HY$ reaction. The transition state of this reaction can be regarded conventionally as a labile formation containing the $X...H...Y$ pseudobond. The characteristics of this bond may influence the activation energy. This influence can be observed with the aid of the IP and MPC models, since each of them makes it possible to convert the activation energy for an individual reaction into the activation energy for a thermally neutral reaction [see Eqns (5) and (10)] and also to take into account the influence of the force constants of the X–H and Y–H bonds on E_{e0} [Eqn (5)]. When the hydrogen abstraction reactions are compared in relation to different classes of compounds, it is useful to employ the parameter r_e , in which the influence of ΔH_e , b_i , and b_f on the activation energy for the reaction has already been taken into account.

In the $X...H...Y$ transition state, the X–Y pseudobond is formed by three electrons. According to the Pauli principle, one molecular orbital may be occupied by only two electrons with opposite spins.²⁹ Two molecular orbitals therefore participate in the transition state: the bonding orbital of the X–Y bond, in which two electrons are accommodated, and its nonbonding orbital containing the third electron. The energy of the nonbonding orbital D_T is higher the stronger the X–Y bond; it is described by the Sato formula⁴⁸

$$D_T = D_e \{ \exp(-bD_e^{-1/2}r) + 0.5 \exp(-2bD_e^{-1/2}r) \}, \quad (33)$$

where D_e and D_T are the energies of the bonding and nonbonding X–Y orbitals respectively, $2b^2$ is the force constant, and r is the amplitude of the vibration of this bond. In the given instance, $r = r_{XH} + r_{YH} + r_e - r_{XY}$. The involvement of the nonbonding orbital of the X–Y bond in the formation of the activation barrier has come to be referred to as triplet repulsion.⁴⁹ This effect constitutes the basis of three semiempirical methods for the

calculation of the activation energies for radical substitution reactions: the ‘bond energy–bond order’ (BEBO) method,^{49, 50} the ‘bond energy–bond length’ (BEBL) method,⁵¹ and the Zavitsas method.^{52–54} In all these methods, the activation energy corresponds to the maxima on the ‘potential energy–bond order’ (BEBO) curves or the ‘potential energy–bond length’ (BEBL, Zavitsas method) curves while the potential energy curve represents a superposition of two Morse curves corresponding to the Y–H and X–H reacting bonds and the curve for the non bonding orbital of the X–Y bond [Eqn (33)].

The role of triplet repulsion in radical abstraction can be clearly traced on comparing reactions in which the energies of the X–Y bonds differ significantly.^{55, 56} The values of E_{e0} and r_e for a series of radical abstraction reactions found by the IP method^{41, 42} as well as the energies D_e of the X–Y bond are presented below.

X...H...Y	E_{e0} /kJ mol ⁻¹	$10^{11} r_e$ /m	D_e /kJ mol ⁻¹
R...H...R	68.2	4.414	382
R...H...N	60.2	3.862	361
PhO...H...OAm	41.8	2.772	~ 0
RO ₂ ...H...O ₂ R	43.1	2.854	88
RO ₂ ...H...OAr	45.3	2.885	~ 0
RO ₂ ...H...OAm	45.6	2.895	~ 0

The difference between the reactions with a high energy of the X–Y (C–C and C–N) bond, for which $E_{e0} \sim 60$ –70 kJ mol⁻¹, and the reactions with a very low energy of this bond (O–O), for which $E_{e0} \sim 40$ –45 kJ mol⁻¹ can be clearly traced. Within the limits of the error of the measurement, the parameter r_e for the last four reactions is constant: $r_e = (2.85 \pm 0.05) \times 10^{-11}$ m. This value is characteristic of reactions with zero triplet repulsion in the transition state. On substituting this quantity in Eqn (5), we obtain the following equation for the estimation of the contribution of triplet repulsion ΔE_T to the activation energy E_{e0} :

$$\Delta E_T = \frac{(b_i b_f)^2}{(b_i + b_f)^2} (r_e^2 - 2.85^2 \times 10^{-22}). \quad (34)$$

For reactions of the $R' + RH$ class, this contribution is 40.0 kJ mol⁻¹, i.e. a considerable proportion of the activation energy $E_{e0} = 68$ kJ mol⁻¹ is due precisely to the triplet repulsion in the transition state.

Another important characteristic of the X–Y bond is its polarity induced by the different electron affinities of the atoms or radicals X and Y.^{27, 55, 56} The greater the difference, the greater the polarity of the bond, its strength and its dipole moment. According to Pauling, the polarity of the X–Y bond may be characterised by the extent to which its strength differs from half the sum of the bond dissociation energies of the XX and YY molecules by virtue of the different electronegativities of the atoms X and Y:

$$\Delta EA(XY) = D_{XY} - 0.5(D_{XX} + D_{YY}). \quad (35)$$

The question arises whether the polarity of the X–Y bond affects the $X' + YH$ radical abstraction reactions. We shall compare two reactions:³⁵ $H' + H_2$ and $Cl' + H_2$.

Reaction	E_{e0} /kJ mol ⁻¹	$10^{11} r_e$ /m	D_{XY} /kJ mol ⁻¹
$H' + H_2$	58.2	3.69	436.0
$Cl' + H_2$	36.7	3.04	431.6

Evidently the dissociation energies of the H–H and Cl–H bonds are very close and the triplet repulsion in the transition states of these reactions is therefore almost identical. Nevertheless the quantities E_{e0} and r_e in these two reactions differ very considerably. The reason for this is that the H–H bond is nonpolar, while the Cl–H bond is polarised and $\Delta EA = 92.3$ kJ mol⁻¹ [Eqn (35)] for the latter. As in the HCl molecule, in the transition state there is evidently a strong attraction between Cl and H, which in fact induces a decrease in r_e and E_{e0} . If the

$H' + HCl$ reactions were characterised by the same parameter $r_e = 3.69 \times 10^{-11}$ m as the $H' + H_2$ reaction, the energy $E_{e0} = 56.5$ kJ mol⁻¹ [Eqn (5)] would have been obtained for it. The difference between the expected and observed activation energies ($\Delta E_{EA} = 36.7 - 56.5 = -19.8$ kJ mol⁻¹) must be attributed to the influence of the unequal electronegativities of the hydrogen and chlorine atoms on E_{e0} in the $H' + HCl$ reaction.

The $R' + RH$ and $RO' + RH$ reactions may serve as another example.^{55, 56}

Reaction	E_{e0} /kJ mol ⁻¹	$10^{11} r_e$ /m	D_{XY} /kJ mol ⁻¹
$R' + RH$	68.2	4.414	376
$RO' + RH$	54.8	3.553	361

In this case, the similarity of the R–R and RO–R bond dissociation energies also leads to the similarity of the triplet repulsion energies in the R...H...R and RO...H...R transition states. However, in these reactions too the quantities E_{e0} and r_e differ appreciably. The polarity of the O–C bond in the $RO' + RH$ reaction is manifested here. On substituting the dissociation energies $D(CH_3-CH_3)$, $D(CH_3O-OCH_3)$, and $D(CH_3-OCH_3)$ in Eqn (35), we obtain $\Delta EA = 80$ kJ mol⁻¹. Calculation of the contribution of the electronegativities of the O and C atoms to the activation energy for the $RO' + RH$ reaction yields $\Delta E_{EA} = -26.1$ kJ mol⁻¹, which should be regarded as very considerable bearing in mind that $E_{e0} = 54.8$ kJ mol⁻¹.

When the fragments X and Y approach one another in the X...H...Y transition state, their outer electron shells begin to repel one another. It is to be expected that the repulsion will be stronger, the larger the radii of the atoms X and Y. The examples presented below confirm this conclusion. We shall compare the $R' + RH$, $R' + HSiR'_3$, and $R_3Si' + HSiR'_3$ reactions.³⁷

Reaction	$10^{11} r_e$ /m	$10^{11} r_{XY}$ /m	D_{XY} /kJ mol ⁻¹	ΔEA /kJ mol ⁻¹
$R' + RH$	4.414	15.13	376	0.0
$R' + HSiR'_3$	4.782	18.70	376	11.0
$R_3Si' + HSiR'_3$	4.967	23.59	354	0.0

An evident parallel variation of the increment in r_e and in the bond length r_{XY} is observed. On the other hand, the strengths of the X–Y bonds in this series are similar, so that the increase in r_e is not caused by a change in the triplet repulsion. The electronegativities of the C and Si atoms are also similar and in the first and third reactions $\Delta EA = 0$.

The empirical dependence of the parameter r_e (in m) on D_{XY} , ΔEA , and r_{XY} in the interaction of radicals carrying a free valence on the C and O atoms with the C–H, O–H, Si–H, and S–H bonds has the following form:³⁷

$$10^{22} r_e^2 = 18 \left[\left(\frac{r_{XY}}{r_{HH}} \right)^{1/2} - 1 \right] + 13.7 \left(\frac{D_{XY}}{D_{HH}} \right) - 22.4 \left(\frac{\Delta EA}{D_{HH}} \right). \quad (36)$$

A similar formula has been proposed³⁷ for reactions with participation of H' :

$$10^{22} r_e^2 = 12.8 \left[\left(\frac{r_{XY}}{r_{HH}} \right)^{1/2} - 1 \right] + 13.7 \left(\frac{D_{XY}}{D_{HH}} \right) - 22.4 \left(\frac{\Delta EA}{D_{HH}} \right). \quad (37)$$

These formulae make it possible to estimate the contribution of each factor — triplet repulsion ΔE_T , electronegativity, ΔE_{EA} , and repulsion ΔE_R of the electron shells of the X and Y atoms in the transition state — to the activation barrier E_{e0} for each class of radical abstraction reactions. Since $E_{e0} = br_e(1 + \alpha)^{-1}$, it follows that, by employing the corresponding increment from Eqns (36) and (37), it is possible to calculate the contribution of a particular factor. Table 6 presents the results of such calculation for 21 classes of radical abstraction reactions.

The influence of the radius of the atom Y on the $X' + HY$ reactions is indicated by the data obtained by the present author.⁴⁶

Table 6. The contributions of triplet repulsion (ΔE_T), the electron affinity of the fragments X and Y (ΔE_{EA}), and the repulsion of the atoms forming the X–Y bond (ΔE_R) to the activation energy E_{e0} for the $X^\bullet + HY$ reaction.

Reaction	$10^{-11} b(1 + \alpha)^{-1}$ /kJ ^{0.5} mol ^{-0.5} m ⁻¹	$10^{11} r_e$ /m	ΔE_T /kJ mol ⁻¹	ΔE_{EA} /kJ mol ⁻¹	ΔE_R /kJ mol ⁻¹
R [•] + HR	1.87	4.41	41	0	25
R [•] + H ₂ NR	2.05	3.84	45	−8	32
R [•] + HOOR	2.06	3.80	37	−7	29
R [•] + HOAr	2.08	3.80	35	−19	26
R [•] + HSiR ₃ '	1.60	4.78	30	−3	27
R [•] + HSR	2.13	4.09	44	0	46
HO [•] + HR	2.09	3.67	53	−22	30
HO [•] + SiH ₄	1.79	3.30	55	−45	28
RO [•] + HR	2.08	3.55	49	−20	30
RO [•] + HSiR ₃ '	1.74	3.68	45	−34	26
RO ₂ [•] + HR	2.06	3.80	37	−7	29
RO ₂ [•] + HOOR	2.30	2.85	15	0	28
RO ₂ [•] + HOAr	2.33	2.88	0	0	45
AmO [•] + HR	2.08	3.66	28	−23	26
AmO [•] + HOAr	2.33	2.77	0	0	42
R ³ Si [•] + HSiR ₃ '	1.38	4.97	18	0	27
H [•] + HR	1.96	3.76	53	−8	10
H [•] + NH ₃	2.11	3.45	63	−21	9
H [•] + H ₂ O	2.20	3.91	76	−43	8
H [•] + SiH ₄	1.69	4.09	34	−2	15
H [•] + H ₂ S	1.88	3.60	42	−5	16

Thus linear dependences of the distance r_e on the radius of the halogen atom (Y) have been observed in the $O^\bullet + HY$ and $HO^\bullet + HY$ (Y = Cl, Br, I) reactions: $r_e = 0.29 r_Y$ and $r_e = 0.32 r_Y$ (IP model). These relations reflect the real contribution of the repulsion of the molecular orbitals of the atoms approaching one another to the formation of the activation barrier.

It is seen from the data presented in Table 6 that the triplet repulsion ΔE_T makes an additional contribution to the activation energy E_{e0} . The reactions in which the X–Y bond is not formed (for example in the $RO_2^\bullet + HOAr$ reaction) are an exception.

The difference between the electronegativities of the fragments X and Y lowers the activation energy. When the discrepancy between the electron affinities is large, this decrease may be very considerable. For example, $\Delta E_{EA} = -45$ kJ mol⁻¹ for the $HO^\bullet + SiH_4$ reaction and $\Delta E_{EA} = -43$ kJ mol⁻¹ in the reaction of H[•] with water.

The repulsion of the electron orbitals of the atoms forming the reaction centre ΔE_R plays an important role in all the radical abstraction reactions. In the interaction of radicals with molecules, the contribution of this repulsion ranges from 25 to 46 kJ mol⁻¹. In reactions of molecules with hydrogen atoms, the contribution is naturally smaller, varying from 8 to 16 kJ mol⁻¹.

Thus Eqns (36) and (37) make it possible to estimate the quantities r_e and E_{e0} for classes of reactions which have not been investigated.

VIII. The causes of the high reactivity of antioxidants

The considerations concerning the influence of physical factors on the heights of activation barriers in radical reactions of compounds in different classes, described above, may be used also to account for the kinetics of specific processes. Two such processes will be examined below: oxidation processes occurring in the presence of phenols and aromatic amines. Phenols and aromatic amines (antioxidants) react very rapidly with peroxy radicals, whereas $RO_2^\bullet$ interaction with hydrocarbons is comparatively slow.⁵⁷ We shall compare three reactions: (a) $RO_2^\bullet + C_6H_5CH_2CH_3$, (b) $RO_2^\bullet + 4-CH_3C_6H_4OH$, and (c) $RO_2^\bullet +$

$(4-CH_3C_6H_4)_2NH$, where $RO_2^\bullet$ is a secondary peroxy radical.^{28, 38, 39}

Reaction	$k(333\text{ K})$ /litre mol ⁻¹ s ⁻¹	ΔH /kJ mol ⁻¹	$10^{-7} A$ /litre mol ⁻¹ s ⁻¹	E /kJ mol ⁻¹
(a)	2.0	−8.5	2.0	44.6
(b)	1.4×10^4	−7.7	3.0	21.4
(c)	3.0×10^5	−8.0	3.0	16.1

Evidently the peroxy radical reacts with the O–H bond of *p*-cresol faster by four orders of magnitude and with the N–H bond of bis(*p*-tolyl)amine faster by five orders of magnitude than with the C–H bond of ethylbenzene. Furthermore the enthalpies ΔH of these reactions are very similar and so are the pre-exponential factors. The large difference between the rate constants is determined exclusively by the inequality of the activation energies E , which indicates in its turn that the quantities E_{e0} are different. This question has been analysed using the IP⁵⁸ and MPC⁵⁹ models. The correlation equation (36) makes it possible to establish the causes of this difference. The values of E_{e0} (kJ mol⁻¹), $10^{-11} b(1 + \alpha)^{-1}$ (kJ^{0.5} mol^{-0.5} m⁻¹), $10^{11} r_e$ (m), and the increments ΔE_R , ΔE_T , and ΔE_{EA} (kJ mol⁻¹) calculated by Eqn (36) are presented below.

HY	E_{e0}	$10^{-11} b(1 + \alpha)^{-1}$	r_e	ΔE_R	ΔE_T	ΔE_{EA}
RH	61.5	1.87	3.80	32	37	−7
ArOH	45.3	2.33	2.88	45	~ 0	0
AmH	39.0	2.16	2.80	44	15	−20

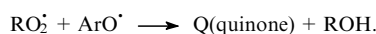
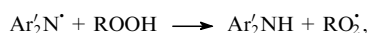
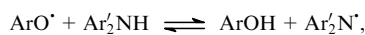
The activation energy for the thermally neutral reaction of $RO_2^\bullet$ with the C–H bond is indeed greater than in the interaction of the same radical with the O–H bond of the phenol and the N–H bond of the amine. In the case of the phenol, the comparatively low value of E_{e0} is caused by the absence of triplet repulsion (the ArO–OAr bond is very weak), while in the case of the amine the large difference between the electronegativities of the N and O atoms, which leads to the polarisation of the N...H...O reaction centre and a decrease in the activation energy for low triplet repulsion, may be regarded as such a cause. On the other hand, the high value of E_{e0} in the reactions of $RO_2^\bullet$ with the C–H bond of the hydrocarbon is caused primarily by the strong triplet repulsion

($\Delta E_T = 37 \text{ kJ mol}^{-1}$) and also by the comparatively slight polarisation of the C–O bond ($\Delta E_{EA} = -7 \text{ kJ mol}^{-1}$).

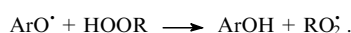
Aminyl radicals interact extremely rapidly with the O–H bond.^{60,61} For example, the rate constants for the abstraction of the H atom from phenol at 294 K is $1 \times 10^6 \text{ litre mol}^{-1} \text{ s}^{-1}$, whereas the enthalpy of this reactions is only 2 kJ mol^{-1} . The high selective reactivity of aminyl radicals in the abstraction of H atoms from the O–H bond is indicated by the comparison of the values of E_{e0} for the $\text{Am}^\bullet + \text{HY}$ reactions:⁴³

HY	RH	ArOH	AmOH	ROOH
$E_{e0} / \text{kJ mol}^{-1}$	81.7	27.6	33.2	41.1

It is seen from the data presented that the activation energy for the thermally neutral reaction involving the abstraction of H from the O–H bond is smaller by $40\text{--}54 \text{ kJ mol}^{-1}$ than for the abstraction of H from a C–H bond of the hydrocarbon. The reason for this difference is the high polarity of the O–N bond in the transition state for weak triplet repulsion. By virtue of this precise factor, aromatic amines are effective catalysts of the reaction of the phenoxyl radical with a hydroperoxide.⁶²



This process is faster than the forward reaction



For the same reason (the polarity of the N–O bond), aromatic amines can ensure multiple chain termination in the oxidation of alcohols, alkenes, and polymers, where the $\text{>C(OH)O}_2^\bullet$ and $\text{HO}_2^\bullet$ radicals participate in chain propagation. This is not observed in the oxidation of hydrocarbons. This question has been discussed in detail in another review by the present author.⁶³

IX. The influence of the π -bond and the steric effect

An aromatic ring and a double or triple bond in the α -position relative to a C–H bond weaken the latter by virtue of the delocalisation of the unpaired electron in its interaction with the π -bond. The weakening of the C–H bond is very considerable: for example, $D(\text{C–H})$ is 418 kJ mol^{-1} in ethane, 363 kJ mol^{-1} in the methyl group of propene, and 368 kJ mol^{-1} in the methyl group of toluene. Such decrease in the strength of the C–H bond diminishes the enthalpy of the radical abstraction reaction and hence its activation energy. This effect is illustrated below in relation to the reactions of the methyl radical with hydrocarbons.²⁷

Hydrocarbon	C_2H_6	$\text{CH}_3\text{CH}=\text{CH}_2$	$\text{C}_6\text{H}_5\text{CH}_3$
$\Delta H / \text{kJ mol}^{-1}$	–20.0	–75.2	–70.2
$E / \text{kJ mol}^{-1}$	52.4	37.4	39.3

Comparative analysis of the kinetics of the reactions of atoms and radicals with paraffinic (R^1H), olefinic (R^2H), and aromatic alkyl-substituted (R^3H) hydrocarbons within the framework of the IP and MPC models permitted a new important conclusion. It was found that the π -C–C bond occupying the α -position relative to the attacked C–H bond increases the activation energy for thermally neutral reaction.²⁷ The corresponding results are presented in Table 7. Evidently the activation energy for a thermally neutral reaction with participation of a hydrogen atom or a radical (alkyl, alkoxyl, *etc.*) is higher in those cases where there is a π -bond or an aromatic ring next to the attacked C–H bond. This result is independent of the method used to calculate (IP or MPC) the parameters br_e and E_{e0} . Evidently this effect is a property of the structures themselves and the π -bond exerts a dual effect on the reaction centre. On the one hand, by weakening the C–H bond the π -bond in the α -position lowers the enthalpy and hence the activation energy for the reaction. On the other hand, by interacting with the electrons of the reacting bonds, the π -orbital increases the strength of the C–Y bond in the $\text{Y}^\bullet + \text{HR}$ reaction, which increases the energy of the non bonding C–Y orbital and intensifies triplet repulsion.

The influence of bulky substituents, for example tertiary alkyl groups, on the kinetics of diverse chemical reactions is well known. A steric effect occurs also in radical reactions. Such substituents usually influence both the enthalpy of the reaction and its activation energy. The IP and MPC models examined in the present review make it possible to separate these effects and to estimate separately the contribution of steric hindrance to the activation energy.²⁷ We shall examine the thoroughly investigated radical reactions in which a radical attacks the O–H group of a sterically hindered phenol (Ar^2OH) containing two *tert*-alkyl (as a rule *tert*-butyl) groups in the *ortho*-position relative to the phenolic group. Comparison of the energies E_{e0} for isotypical reactions involving both sterically unhindered (Ar^1OH) and sterically hindered (Ar^2OH) phenols makes it possible to estimate the contribution of steric hindrance ΔE_s to the activation energy:

$$\Delta E_s = E_{e0}(\text{Ar}^2\text{OH}) - E_{e0}(\text{Ar}^1\text{OH}). \quad (38)$$

The results of the comparison are presented in Table 8. The steric hindrance increases the activation energy for a thermally neutral reaction by 8.2 ± 2.0 , 8.2 ± 1.5 , and 24 kJ mol^{-1} when oxygen-centred, nitrogen-centred, and alkyl radicals are involved respectively. The data obtained with the aid of the IP and MPC

Table 7. The influence of the π -C–C bond on the activation thermally neutral radical abstraction reactions.^{14, 27, 64–68}

Radical	RH	IP model			MPC model		
		$br_e / \text{kJ}^{0.5} \text{ mol}^{-0.5}$	$E_{e0} / \text{kJ mol}^{-1}$	$\Delta E_\pi / \text{kJ mol}^{-1}$	$br_e / \text{kJ}^{0.5} \text{ mol}^{-0.5}$	$E_{e0} / \text{kJ mol}^{-1}$	$\Delta E_\pi / \text{kJ mol}^{-1}$
$\text{H}^\bullet$	R^1H	14.49	57.9		19.45	66.1	
	R^2H	15.58	66.9	9.0	20.44	71.4	5.3
	R^3H	15.34	64.9	7.0	19.91	69.1	3.0
$\text{R}^\bullet$	R^1H	17.23	74.2		21.86	71.3	
	R^2H	18.86	88.9	14.7	24.87	82.9	11.6
	R^3H	18.11	82.0	7.8	22.53	73.3	2.0
$\text{RO}^\bullet$	R^1H	13.37	55.2		16.98	58.5	
	R^2H	14.41	64.1	8.9	19.99	75.4	16.9
	R^3H	14.16	61.9	6.7	18.17	65.1	6.6
$\text{RO}_2^\bullet$	R^1H	14.23	61.5		18.24	61.8	
	R^2H	15.68	74.7	13.2	20.37	72.9	11.1
	R^3H	14.74	66.0	4.5	19.21	66.8	5.0
$\text{AmO}^\bullet$	R^1H	13.72	58.0				
	R^2H	15.66	75.5	17.5			
	R^3H	14.42	64.0	6.0			

Table 8. The contributions of the steric effect (ΔE_S) to the activation energies for thermally neutral reactions of sterically hindered phenols, phenoxy radicals, and diphenylpicryl hydrazyl.^{38, 41, 43, 59}

Reaction	IP method			MPC method		
	br_e /kJ ^{0.5} mol ^{-0.5}	E_{e0} /kJ mol ⁻¹	ΔE_S /kJ mol ⁻¹	br_e /kJ ^{0.5} mol ^{-0.5}	E_{e0} /kJ mol ⁻¹	ΔE_S /kJ mol ⁻¹
RO ₂ [•] + Ar ¹ OH	13.76	45.3		16.58	45	
RO ₂ [•] + Ar ² OH	14.40	51.8	6.5	18.26	52.0	7.0
CH ₃ [•] + Ar ¹ OH	17.38	59.8				
CH ₃ [•] + Ar ² OH	18.92	84.2	24.4			
Ar ¹ O [•] + Ar ¹ OH	12.61	39.7				
Ar ¹ O [•] + Ar ² OH	13.31	44.3	4.6	17.19	48.5	
Am [•] + Ar ¹ OH	10.93	27.6		12.84	28.0	
Am [•] + Ar ² OH	12.15	34.2	6.6	14.99	36.0	8.0
AmO [•] + Ar ¹ OH	12.93	41.8		16.22	43.8	
AmO [•] + Ar ² OH	14.54	52.9	11.1	19.05	55.8	12.0
Ar ¹ O [•] + HOOR	13.46	45.3		15.86	43.1	
Ar ² O [•] + HOOR	14.40	51.8	6.5	18.26	52.0	
Ar ² O [•] + Ar ² OH	14.37	51.6	7.3	19.13	56.7	8.2
Ar ¹ O [•] + AmH	10.13	27.6		11.90	28.0	
Ar ² O [•] + AmH	11.59	36.2	8.6	14.49	38.8	10.8
Am [•] + RH	16.87	81.7		22.57	80.6	
DPPH [•] + RH	18.59	99.3	17.6	26.76	98.7	18.1
DPPH [•] + Ar ¹ OH	14.85	51.0	23.4	18.71	51.9	23.9
DPPH [•] + Ar ² OH	16.74	64.8	30.6	21.63	64.3	28.3

models in most cases agree. The steric effect is manifested similarly also in the reactions of sterically hindered (Ar²O[•]) phenoxy radicals with various substrates (Table 8). The reactions of the sterically hindered diphenylpicryl radical (DPPH[•]) and the unhindered diphenylaminyl radical may serve as another example (Table 8). In the reactions of DPPH[•] with phenols, the contribution of the steric effect to E_{e0} ranges from 23 to 30 kJ mol⁻¹, *i.e.* is very considerable.

X. The polar effect in radical reactions

An extensive literature has been devoted to polar effects in chemical reactions.^{69–72} The IP and MPC models permit a fresh approach to this important problem. The introduction of a functional group into a hydrocarbon molecule alters the dissociation energy of the neighbouring C–H bonds, which is indicated by the examples presented below (the bond strengths taken from the review of McMillen and Golden⁷³).

Compound	C ₂ H ₆	C ₂ H ₅ OH	CH ₃ CHO	C ₂ H ₅ OC ₂ H ₅
D /kJ mol ⁻¹	418.4	392.5	365.3	383.7

The change in the C–H bond strength affects the enthalpies and through them the activation energies for radical abstraction reactions. If a molecule is attacked by a nonpolar group (hydrogen atom, alkyl radical), then the influence of the polar group on the activation energy is confined to a change in ΔH . This has been confirmed by data on the reactions of the methyl radical with the C–H bonds of hydrocarbons and their derivatives (alcohols, ethers, *etc.*),¹² which are characterised by a virtually identical parameter $br_e = 17.23$ kJ mol⁻¹. A similar result has been obtained when the MPC model was used.⁴⁷ Thus a polar group (OH, OR, *etc.*) influences only the enthalpy of reaction and not the energy of the reaction centre of a transition state of the type C...H...C and H...H...C.

A different picture is observed when a polar radical reacts with a C–H bond of a polar molecule. For example, the reaction of an oxygen atom with a methane C–H bond is characterised by the parameter $br_e = 13.11$ kJ^{0.5} mol^{-0.5} while the reaction with a methanol C–H bond is characterised by the corresponding parameter of 12.55 kJ^{0.5} mol^{-0.5}. For these values of br_e , the difference between the activation energies is 4.6 kJ mol⁻¹. The decrease in activation energy can be explained by the fact that the

polar OH group in the O...H...C–OH transition state interacts with the O...H...C polar reaction centre.

The IP and MPC models make it possible to isolate from the overall effect of the substituent its contribution to E . In the calculation, use is made of the values of ΔH and the activation energy for a thermally neutral reaction of the given group (reaction series), because the activation energy can be represented by the sum $E_e = E_{e0} + \Delta E_H$ (see above), where the second term takes into account only the influence of enthalpy. The polar interaction in the transition state may be inferred by comparing the values of E_{e0} in various reactions involving a hydrocarbon and the corresponding polar molecule. The contribution of the polar interaction to the activation energy (ΔE_μ) can be estimated²⁷ from the formula

$$\Delta E_\mu = \frac{(br_e)_\mu^2 - (br_e)_{RH}^2}{(1 + \alpha)^2}, \quad (39)$$

where the parameters $(br_e)_\mu$ and $(br_e)_{RH}$ refer to reactions involving a polar compound YH and a reference hydrocarbon RH respectively. The results of the calculation of the energy ΔE_μ (in kJ mol⁻¹) for the X[•] + HY gas-phase reactions are presented below:⁷⁴

X [•]	HY				
	CH ₃ OH	CH ₂ O	RCHO	CH ₃ COCH ₃	(CH ₃) ₂ O
O [•]	4.6	−4.6	−7.9	−9.4	−5.1
HO [•]	2.4	1.8	1.5	−11.4	2.8
CH ₃ O [•]	−6.0	0	−12.2	−	−
(CH ₃) ₃ CO [•]	−	−4.2	−3.1	−17.8	−

Extensive data concerning the influence of polar groups on the activation energies for abstraction reactions have been obtained by analysing experimental data on reactions with participation of alkoxy and peroxy radicals in the liquid phase.^{75–77} These data are presented in Table 9. As can be seen from the table, the interaction of a polar group with a O...H...C or O–O...H...C polar reaction centre can both diminish and increase the activation energy. A very marked decrease in activation energy (from −11 to −19 kJ mol⁻¹) has been observed in the reactions of RO[•] and RO₂[•] with aldehydes and ketones. The alcoholic group diminishes slightly the height of the activation barrier (by 1–3 kJ mol⁻¹), the reaction of RO[•] with benzyl alcohol being

Table 9. Kinetic parameters of the reactions of alkoxy and peroxy radicals with the C–H bonds of oxygen-containing compounds YH.^{74–77}

YH	RO [•]		RO ₂ [•]		YO ₂ [•]		
	br_e /kJ ^{0.5} mol ^{−0.5}	ΔE_μ /kJ mol ^{−1}	br_e /kJ ^{0.5} mol ^{−0.5}	ΔE_μ /kJ mol ^{−1}	br_e /kJ ^{0.5} mol ^{−0.5}	ΔE_μ /kJ mol ^{−1}	$\Delta\Delta E_\mu$ /kJ mol ^{−1}
AlkOH	13.36	−1.5	13.71	−2.2	14.52	−5.8	−3.6
cyclo-C ₆ H ₁₁ OH	13.41	−1.1	13.63	−2.2	14.55	−5.6	−3.4
C ₆ H ₅ CH ₂ OH	13.03	−8.8	15.02	−2.8	41.75	−12.7	−9.9
C ₆ H ₅ CHO	11.76	−19.0	13.69	−8.2	13.53	−15.8	−7.6
RCHO	12.56	−12.2	12.83	−8.8	11.76	−15.8	−7.0
RC(O)CH ₂ R	13.17	−10.6	13.66	−15.4	13.96	−13.0	−2.4
RC(O)CHR ₂			13.65	−15.7	12.96	−21.2	−5.5
C ₆ H ₅ CH ₂ C(O)R	13.82	−5.2	14.19	−11.2	13.91	−12.9	−1.7
(RCH ₂) ₂ O	13.34	−1.7	14.30	3.4	14.52	5.7	2.3
(R ₂ CH) ₂ O	13.81	2.3	14.57	6.3	14.25	3.5	−2.8
(C ₆ H ₅ CH ₂) ₂ O			14.55	−1.4			
(C ₆ H ₅ RCH) ₂ O			15.49	6.1	15.21	3.7	−2.4
(RO) ₂ CH ₂	13.07	−3.9	14.06	1.8	14.00	1.4	−0.4
(RO) ₂ CHCH ₃	13.50	−0.4	14.52	6.2	14.25	3.8	−2.4
cyclo-C ₆ H ₁₁ OCH ₃			14.76	8.4			
			13.43	−3.8	13.43	−3.8	0.0
			13.42	−3.4	13.20	−5.3	−1.9
			13.54	−2.4	13.81	−0.2	2.2
CH ₃ OC(O)R	14.28	6.3	15.10	8.7			
RCH ₂ OC(O)R	14.47	8.0	15.00	8.9	13.48	−11.2	−20.1
cyclo-C ₆ H ₁₁ OC(O)CH ₃	12.79	−6.1	14.89	8.8			—
C ₆ H ₅ CH ₂ OC(O)R	13.77	−2.7	15.11	4.5	14.04	−17.6	−22.1
CH ₃ C(O)OH			15.33	11.5			
RCH ₂ C(O)OH			14.92	7.9			
(CH ₃) ₂ CHC(O)OH			15.08	10.6			
RCH ₂ C(O)OR			13.82	−2.7			
(CH ₃) ₂ CHOR			14.36	2.7			
C ₆ H ₅ CH ₂ C(O)OR	13.17	−3.1	13.80	−7.6			

an exception. In the reactions with ethers, an increase in activation energy is observed.

XI. The effect of multipole interaction

Yet another effect, namely multipole interaction, is manifested in the reactions of polar radicals with polyfunctional compounds.⁷⁸ This effect consists in the unequal reactivities of the same group, for example >CH(OH), in compounds with one and several functional groups. Factual data concerning multipole interactions have been examined in a review.⁷⁹ The corresponding kinetic data have been analysed within the framework of the IP model.⁷⁷ The multipole interaction is manifested, in particular, in the reactions of peroxy radicals RO₂[•] containing functional groups, with oxygen-containing compounds YH (Table 9). The magnitude of this effect in the transition state may be inferred from the change in the activation energy for a thermally neutral reaction on passing from a monofunctional compound YH to a polyfunctional compound ZH:

$$\Delta\Delta E_\mu = \frac{(br_e)_{ZH}^2 - (br_e)_{YH}^2}{(1 + \alpha)^2}.$$

As can be seen from Table 9, the highest values of $\Delta\Delta E_\mu$ correspond to the transition from RO₂[•] to YO₂[•] containing a carbonyl or ester group. Apparently this effect is induced by the dipole–dipole interaction in the transition state. Table 10 presents data concerning the influence of ester groups on the reactivity of CH₂ groups in reactions with peroxy radicals. The

multipole effect always reduces the activation energy for reactions of this group and in certain cases the decrease is extremely significant (down to −10 kJ mol^{−1} and even further).

XII. Solvation of the reactants in radical abstraction reactions

Yet another important effect, observed when reactions take place in the liquid phase, is associated with the solvation of the reactants. Theoretical comparison has shown that the collision frequencies of the species in a gas and in a liquid are different, the difference being due to the difference between the free volumes.⁸⁰ In a gas, the free volume is virtually equal to the volume occupied by the gas species ($V_f \approx V$), while in a liquid it is much smaller than the volume of the liquid species ($V_f \ll V$). Since the motion and collision of the species occur in the free volume, the collision frequency in a liquid is higher than in a gas by an amount $(V/V_f)^{1/3} \approx 4–2$. The activation energies for the reactions of radicals and atoms with hydrocarbon C–H bonds in a gas and in a liquid are virtually identical, that in a liquid being independent of the solvent polarity. This also applies to the parameter br_e (the IP model), which can be seen from the following examples referring to the interaction of the hydroxyl radical with hydrocarbons:⁷⁴

RH	C ₂ H ₆	C ₃ H ₈
br_e (gas) /kJ ^{0.5} mol ^{−0.5}	13.74	13.52
br_e (H ₂ O) /kJ ^{0.5} mol ^{−0.5}	13.48	13.40

Table 10. Kinetic parameters of the reactions of cumenylperoxyl radicals with compounds containing ester groups.⁷⁷

Ester	ΔH_e /kJ mol ⁻¹	E_e /kJ mol ⁻¹	br_e /kJ ^{0.5} mol ^{-0.5}	ΔE_μ /kJ mol ⁻¹	$\Delta\Delta E_\mu$ /kJ mol ⁻¹
[CH ₃ OC(O)] ₂	31.7	72.5	13.70	-3.6	-12.3
[CH ₃ (CH ₂) ₄ C(O)OCH ₂] ₂	23.7	71.0	14.02	0.3	-8.6
[CH ₃ (CH ₂) ₄ C(O)OCH ₂ CH ₂] ₂ O	23.7	68.8	13.73	-0.4	-9.3
CH ₃ O(O)C(CH ₂) ₃ C(O)OCH ₂ CH ₃	23.7	74.8	14.46	2.2	-6.7
[CH ₂ C(O)O(CH ₂) ₂ CH ₃] ₂ CH ₂	23.7	76.6	14.67	6.0	-2.9
[CH ₂ C(O)O(CH ₂) ₃ CH ₃] ₂ CH ₂	23.7	76.1	14.61	5.5	-3.4
[CH ₃ CH ₂ C(O)OCH ₂] ₂ C(CH ₃) ₂	23.7	78.6	14.89	8.0	-0.9
[CH ₃ (CH ₂) ₃ C(O)OCH ₂] ₄ C	23.7	76.8	14.69	6.2	-2.7
[CH ₃ (CH ₂) ₆ C(O)OCH ₂ CH ₂] ₂ O	23.7	77.3	14.72	6.5	-2.4
[CH ₃ C(O)OCH ₂] ₄ C	23.7	77.6	14.78	7.0	-1.9
[CH ₃ CH ₂ C(O)OCH ₂] ₄ C	23.7	75.8	14.55	5.1	-3.8
[CH ₃ (CH ₂) ₈ C(O)OCH ₂] ₄ C	23.7	69.6	13.85	-1.1	-10.0
[CH ₃ CH ₂ C(O)OCH ₂] ₃ CCH ₂ CH ₃	23.7	77.4	14.76	6.8	-2.1

A different picture is observed when a polar molecule is attacked by a polar radical (HO•, RO•, RO₂•). The reaction in a polar solvent is slower than in a nonpolar hydrocarbon solution or in the gas phase. From the change in the parameter br_e , it is possible to estimate the extent to which the activation energy increases as a result of the solvation of the polar reactants:⁷⁴

$$\Delta E_{\text{sol}} = \frac{(br_e)_l^2 - (br_e)_g^2}{(1 + \alpha)^2}. \quad (40)$$

The subscripts l and g in Eqn (40) refer to the liquid and gas phases respectively. The results of the comparison are presented in Table 11. If the HO• + YH reaction takes place in aqueous solution and not in the gas phase, the parameter br_e and hence the activation energy increase. This is associated with the solvation of the reactants and the need to overcome the solvation shell by the reacting component in order to effect the elementary step. The contribution of ΔE_{sol} is particularly large in the reaction of the hydroxyl radical with aldehydes.

When a radical or atom attacks a polar O–H or N–H bond, the reactant Y forms a hydrogen bond of the type O–H...Y or N–H...Y in polar solvents.^{81, 82}

The hydrogen bond shields the reactant and slows down the reaction regardless of what kind of radical — polar or nonpolar — attacks it. A universal kinetic scale has been proposed⁸³ for the estimation of the effectiveness of such shielding. This problem has been examined in detail in a monograph.⁸⁴

Table 11. The contributions of the solvation effect to the activation energies for radical reactions.⁷⁴

RH	$(br_e)_g$ /kJ ^{0.5} mol ^{-0.5}	$(br_e)_l$ /kJ ^{0.5} mol ^{-0.5}	ΔE_{sol} /kJ mol ⁻¹
HO• + RH reaction (in water)			
CH ₃ OH	13.91	14.26	3.1
CH ₃ CH ₂ OH	13.48	14.01	4.6
(CH ₃) ₂ CHOH	13.31	14.12	7.1
(CH ₃) ₃ COH	13.39	14.13	6.5
CH ₃ OCH ₃	13.95	14.70	6.8
(C ₂ H ₅) ₂ O	13.47	14.33	7.6
CH ₂ O	13.84	14.98	10.4
CH ₃ CHO	13.81	14.99	10.8
CH ₃ COCH ₃	13.81	14.50	6.3
CH ₃ COOCH ₃	14.38	14.97	5.5
(CH ₃) ₃ CO• + RH reaction (in CH ₃ COCH ₃)			
CH ₃ COCH ₃	12.67	13.17	7.2

XIII. Estimation of bond strength from kinetic data

The IP and MPC methods make it possible to calculate correctly the dissociation energies of bonds subjected to radical attack.^{85, 86} The parameter br_e and the enthalpy of reaction $\Delta H_{e,\text{min}} < \Delta H_e < \Delta H_{e,\text{max}}$ (see above) are used in such calculations. In order to increase the accuracy of the calculation, the rate constants for two different reactions (l and i) are measured by one method. Within the limits of the same reaction series, the pre-exponential factor calculated per reacting bond remains constant, so that the difference between the activation energies for reactions with participation of the reactants R^lH and RⁱH is

$$\Delta E_{e,i} = E_{e,i} - E_{e,l} = RT \ln \frac{n_i k_l}{n_l k_i}. \quad (41)$$

In the IP model, the relation between E and ΔH is described by Eqns (2)–(4). The following relation between the bond strength difference $\Delta D_i = D_i - D_l$ and $\Delta E_{e,i}$ follows from them:

$$\Delta D_i = \frac{2br_e}{\alpha^2} (E_{e,i}^{1/2} - E_{e,l}^{1/2}) - \left(\frac{1}{\alpha^2} - 1 \right) \Delta E_{e,i}. \quad (42)$$

For $\alpha = 1$, where the force constants of the reacting bonds are identical and $\Delta E_{e,i} \ll E_{e,l}$, we obtain

$$E_{e,i}^{1/2} = \frac{1}{2} br_e + \frac{\Delta H_e}{2br_e} \quad \text{and} \quad E_{e0}^{1/2} = \frac{1}{2} br_e.$$

For a single reaction series, $\Delta D_i = \Delta H = \Delta H_e$, whereupon

$$E_{e,i}^{1/2} - E_{e,l}^{1/2} = \frac{\Delta D_i}{2br_e} = \frac{\Delta D_i}{4E_{e0}^{1/2}}.$$

Since

$$E_{e,i}^{1/2} = (E_{e,l} + \Delta E_i)^{1/2} = \left[E_{e,l} \left(1 + \frac{\Delta E_i}{E_{e,l}} \right) \right]^{1/2} \approx E_{e,l}^{1/2} \left(1 + \frac{\Delta E_i}{2E_{e,l}} \right),$$

it follows that

$$E_{e,i}^{1/2} - E_{e,l}^{1/2} = \frac{\Delta E_i}{2E_{e,l}^{1/2}}.$$

Hence

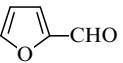
$$\frac{\Delta E_i}{2E_{e,l}^{1/2}} = \frac{\Delta D_i}{4E_{e0}^{1/2}},$$

and the following simple formula is obtained:

$$\Delta D_i = 2 \left(\frac{E_{e0}}{E_{e,1}} \right)^{1/2} \Delta E_{ei} . \quad (43)$$

Eqns (42) and (43) are applicable to reactions in the same reaction series for which $\Delta H_{e,\min} < \Delta H_e < \Delta H_{e,\max}$ [Eqns (28) and (29) and Table 3]. In the case of very exothermic reactions ($\Delta H_e < \Delta H_{e,\min}$), the activation energy is independent of the enthalpy, while for endothermic reactions ($\Delta H_e > \Delta H_{e,\max}$) we have $\Delta E = \Delta D_i$. This method has been used to estimate the strength of the C–H bonds in hydrocarbons⁸⁵ and oxygen-containing compounds,⁸⁶ the O–H bonds in phenols⁸⁷ and hydroxylamines,⁴⁵ the N–H bonds in amines,⁴⁶ and the C–Cl, C–Br, and C–I bonds in halogen-containing compounds.⁸⁸

Table 12. Dissociation energies of the C–H bonds in oxygen-containing compounds estimated by the IP⁸⁷ and MPC⁹⁰ methods.

Compound	<i>D</i> /kJ mol ^{−1}		
	IP	MPC	literature data
CH ₃ CH ₂ OH	391.7±1.1	389.1±0.5	392.5
(CH ₃) ₂ CHOH	382.2±1.2	376.6±0.8	380.7
HOCH ₂ CH ₂ OH	390		385.3
HOCH ₂ (CH ₂) ₂ CH ₂ OH	389.5		
cyclo-C ₆ H ₁₁ OH	375.4	378.6±0.8	
C ₆ H ₅ CH ₂ OH	363.8±0.5	355.3	
C ₆ H ₅ CH(CH ₃)OH	353.8±2.1	353.7	
CH ₃ COCH ₃	394.1±0.9	395.9±0.7	389.1
CH ₃ COCH ₂ CH ₃	386.1±2.1		386.2
CH ₃ COCH(CH ₃) ₂	381.8±2.4		
	377.8	379.6	
C ₆ H ₅ COCH ₃		372.8	
C ₆ H ₅ COCH ₂ CH ₃		367.3±0.1	
C ₆ H ₅ COCH(CH ₃) ₂	336.8	358.2	
(C ₆ H ₅ CO) ₂ CH ₂	343.9		
(C ₆ H ₅ CH ₂) ₂ CO	356.1		
C ₆ H ₅ COCH(OH)C ₆ H ₅	329.1		
	382.6±2.7	385.3±1.1	
HCHO	377.1	379.7	369.4
CH ₃ CHO	377.9	376.7	365.3
C ₆ H ₅ CHO	339.6±1.5		
CH ₃ COOH	390.7±0.5	391.8±1.3	
(CH ₃) ₂ CHCOOH	378.7±0.5	380.4±0.7	
cyclo-C ₆ H ₁₁ COOH	377.8		
(CH ₃ CH ₂) ₂ O	386.8		386.2
ROCOCH ₃	394.8	395.0±0.3	389.1
ROCOCH ₂ R	388.3±0.7	388.4	
ROCOCHR ₂	384.1	381.1±0.6	

A similar method has been developed on the basis of the MPC model.⁸⁶ In order to calculate the dissociation energy of the attacked bond, a system of two equations, one of which refers to the *i*th reaction and the other to the reference reaction 1, is solved numerically (for *D_{e,i}*):

$$br_e + D_{e,1}^{1/2} \ln \left[1 - \left(\frac{E_{e,1}}{D_{e,1}} \right)^{1/2} \right] + \alpha D_{e,1}^{1/2} \ln \left[1 - (E_{e,1} - \Delta H_{e,1})^{1/2} \right] = 0 , \quad (44)$$

$$br_e + D_{e,i}^{1/2} \ln \left[1 - \left(\frac{E_{e,i}}{D_{e,i}} \right)^{1/2} \right] + \alpha D_{e,i}^{1/2} \ln \left[1 - (E_{e,i} - \Delta H_{e,i})^{1/2} \right] = 0 . \quad (45)$$

By solving Eqn (45), the value of *E_{e,i}* is found and then *D_{e,i}* is obtained taking into account the equality *E_{e,i}* = *E_{e,1}* + Δ*E_{e,i}*. The method has been used to calculate the dissociation energies of the C–H bonds in hydrocarbons⁸⁹ and oxygen-containing compounds.⁹⁰ Table 12 presents the values of *D*(C–H) calculated by the two methods from experimental data. These results agree well with one another. The average error in the estimation of Δ*D_i* by the IP and MPC methods is 2 and 1.6 kJ mol^{−1} respectively. The estimate by the MPC method is more accurate, but it is applicable to a narrower range of variation of Δ*E_i* (from −20 to +25 kJ mol^{−1}) than in the IP method (from −30 to +50 kJ mol^{−1}). Both methods make it possible to estimate Δ*D_i* more accurately than by the Polanyi–Semenov method.

XIV. Characteristic features of bimolecular reactions with high absolute enthalpies

The activation energies for highly exothermic radical reactions are known to be virtually zero. The disproportionation of alkyl radicals belongs to such reactions. The rate constants for reactions of this kind and the temperature ranges in which *k* = const are presented below.

Reaction	10 ^{−9} <i>k</i> /litre mol ^{−1}	<i>T</i> /K	Ref.
Me• + Et•	1.15	300–800	91
Me• + Me ₂ CH•	4.53	300–2500	92
Et• + Et•	1.40	300–1200	93
Et• + Me ₂ CH•	2.51	300–2500	92

In a liquid, such fast reactions are limited by the frequency of the diffusional encounters and their activation energies are characteristic of the diffusion of species in a liquid. The IP and MPC models agree with this observation. According to the IP model, each group of reactions is characterised by the parameter *br_e* = const. The lower the value of Δ*H_e*, the lower the position of the point of intersection of the parabolic potential curves on the potential energy axis (Fig. 4). For Δ*H_{e,min}* = Δ*H_e* the curves intersect at the point corresponding to the zero-point vibration energy of the ruptured *i*th bond. At this point, *E_{e0}* + 0.5*hL_{v,i}* and *E* = 0.5*RT*. Such activation energy is retained for all reactions with Δ*H_e* < Δ*H_{e,min}*. Analysis within the framework of the MPC model also leads to a similar result.

The question of the pre-exponential factors for such reactions has been recently examined.⁴⁵ For a separate group of reactions, the quantity *A* calculated for a single attacked bond is virtually constant. For example, for all reactions of the type RO₂• + R¹H, occurring in a hydrocarbon solution (R¹H is an aliphatic hydrocarbon), we have *A* = 10⁸ *n* litre mol^{−1} s^{−1}, where *n* is the number of C–H bonds with equivalent reactivities. This is valid for reactions with Δ*H_{e,min}* < Δ*H_e* < Δ*H_{e,max}*. For Δ*H_e* < Δ*H_{e,min}*, the parameter *r_e* increases with increase in Δ*H_e*, since the potential curves cannot intersect below point *C* (Fig. 4). With increase in *r_e*, the cross-section for the collision of a radical and a molecule and hence also the pre-exponential factor *A* increase. The dependence of *A* on Δ*H* is described by the formula⁴⁵

$$\left(\frac{A}{A_0} \right)^{1/2} = 1 + \beta (|\Delta H_e|^{1/2} - |\Delta H_{e,\min}|^{1/2}) , \quad (46)$$

where *A₀* is a pre-exponential factor typical for the given group of reactions.

The same happens with increase in Δ*H_e*. When the curves intersect at point *L* (Fig. 4), there comes a time when the Δ*H_e* > Δ*H_{e,max}* curves intersect at a distance exceeding the con-

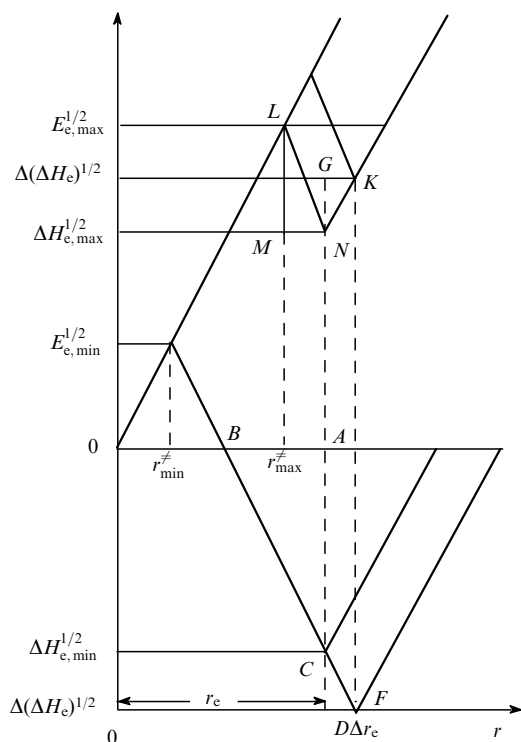


Figure 4. The energy profile for radical abstraction reactions over a wide range of variations of ΔH_c (IP model).⁴⁵ For $\Delta H_{c, \min} < \Delta H_c < \Delta H_{c, \max}$, the parameter $r_e = \text{const}$. Beyond these limits, r_e increases by Δr_e (parabolas with vertices at points K and F).

stant value of r_e for the given group of reactions. For such reactions, $E = \Delta H_c + 0.5RT$, while the pre-exponential factor depends on ΔH_c (Fig. 5).⁴⁵

$$\left(\frac{A}{A_0}\right)^{1/2} = 1 + \beta(|\Delta H_c|^{1/2} - |\Delta H_{c, \max}|^{1/2}). \quad (47)$$

The coefficient $\beta = 1.0$ and 1.6 for reactions with C...H...C and O...H...O reaction centres respectively. Table 3 presents the values of $\Delta H_{c, \min}$ and $\Delta H_{c, \max}$ calculated by Eqns (28) and (29).

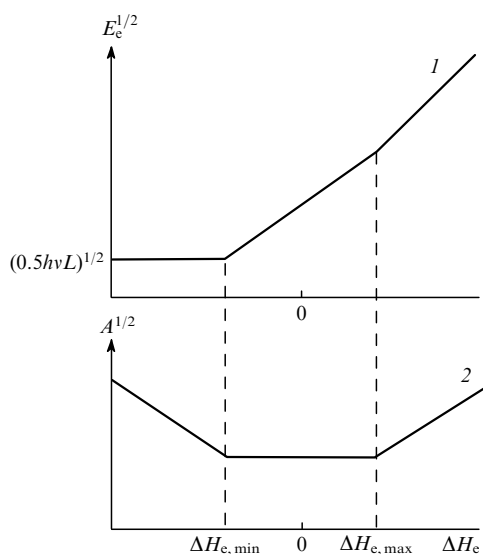


Figure 5. Dependence of E_c (1) and A (2) on ΔH_c according to the IP model.⁴⁵

Evidently the range of H_c in which $A = A_0 = \text{const}$ depends on the parameter br_e and varies within wide limits. Eqns (46) and (47) make it possible to calculate the rate constants for highly exothermic and highly endothermic reactions. As an example, Table 13 presents the results of the calculation of the quantities ΔH , A , and k (at 400 K) for the reactions of a stable nitroxyl radical — 2,2,6,6-tetramethylpiperidinyloxy — with a series of phenols.

Table 13. Dissociation energies of the O–H bonds of phenols and the kinetic parameters of the reactions of 2,2,6,6-tetramethylpiperidinyloxy with various phenols calculated by the Arrhenius equation taking into account Eqn (47).

Phenol	D /kJ mol ⁻¹	E	$10^{-8}A$ /litre mol ⁻¹ s ⁻¹	k (400 K)
<i>p</i> -Cresol	357.8	68.3	9.32	1.12
Hydroquinone	350.3	60.8	10.54	12.12
1-Naphthol	341.4	51.9	1.77	29.65
2-Naphthol	351.8	62.3	6.01	4.40
1-Hydroxy-phenanthrene	352.7	63.2	6.47	3.62
Phenol	367.0	77.5	15.41	0.12
4-Acetylphenol	369.5	80.0	17.25	6.17×10^{-2}
4-Aminophenol	354.7	65.2	7.54	2.31
4-Benzoyloxy-phenol	347.5	58.0	4.00	10.69
4-Bromophenol	370.6	81.1	18.09	4.65×10^{-2}
4-Butoxyphenol	345.8	56.3	3.31	14.71
4- <i>tert</i> -Butyl-phenol	356.9	67.4	8.79	1.39
4-Methoxyphenol	349.0	59.5	4.66	7.93
3,4-Dimethylphenol	352.6	63.1	6.42	3.70
2,6-Dimethylphenol	354.9	65.4	7.65	2.21
4-Nitrophenol	369.7	80.2	17.41	5.86×10^{-2}
4-Phenylphenol	357.4	67.9	9.08	1.24
Pentamethylphenol	338.5	49.0	1.00	39.95
Resorcinol	365.8	76.3	29.12	0.32

XV. Conclusion

Thus the successive employment of the IP and MPC models for the analysis of the reactivities of the reactants in radical abstraction reactions yield very similar results. These models make it possible to divide all radical abstraction reactions into classes and to characterise quantitatively each class by a pair of force constants for the ruptured and generated bonds (b_i and b_f). In both models, these parameters are naturally identical. Each class of reactions may consist of one or several groups of reactions. All the reactions of a given group are characterised by a single parameter r_e and the energy of a thermally neutral reaction E_{c0} . The parameters r_e in the IP and MPC models differ but the values of E_{c0} are very similar. Each individual reaction is additionally characterised by the enthalpy. Thus an individual radical reaction is characterised in both models by four parameters: b_i , b_f , E_{c0} , and ΔH_c . Their number can be reduced to three: $\alpha = b_i/b_f$, $b_i r_e$, and ΔH_c .

Analysis with the aid of the IP and MPC models of extensive experimental data on the kinetics of radical reactions has shown that the reactivities of the interacting molecules and radicals are determined by diverse physical factors. The following 10 factors which determine the height of the potential barrier in radical abstraction reactions have been revealed.

1. The enthalpy of reaction ΔH_c . For low values of this enthalpy, the dependence of the activation energy E_c on ΔH_c assumes the form $E_c^{1/2} = E_{c0}^{1/2} + \alpha \Delta H_c$.

2. The force constants of the ruptured and generated bonds. A correlation between E_{c0} and the force constant of the C–X bond

has been established for the first time in relation to the reactions of a hydrogen atom and alkyl radicals with alkyl halides.

3. The strength of the X–Y bond in the $X^{\bullet} + HY$ reactions. The stronger this bond, the higher the activation energy. This relation is due to triplet repulsion in the transition state when one of three electrons occupies the nonbonding X–Y orbital.

4. The electronegativities of the fragments (radicals) X and Y. The difference between the electronegativities of these fragments (ΔEA) induces their attraction in the transition state, which lowers the activation energy. The quantity ΔE_{e0} is proportional to $-\Delta EA$.

5. The radii of the atoms X and Y, between which a hydrogen atom or some other atom is transferred. The greater the radii, i.e. the longer the X–Y bond, the stronger the repulsion in the transition state, and the greater the activation energy. It has been established empirically that the quantity ΔE_{e0} is proportional to $r_{X-Y}^{1/2}$.

6. The presence of a polar group in the molecule or radical. It influences the activation energy if the reaction centre is also polar ($\Delta EA \neq 0$). Both models make it possible to separate the influence of the polarity of the X–Y bond on the enthalpy of reaction (the polar factor) and the influence of the polar group on the activation energy for a thermally neutral reaction and also to estimate the contribution of each factor to the activation energy.

7. The presence of several polar groups in the molecule. In this case, the multidipole interaction effect, influencing the activation energy, arises. This effect differs significantly from the influence of a single polar group on the activation energy.

8. The presence of a π -bond or an aromatic ring in the α -position relative to the attacked C–H bond. The activation energy E_{e0} increases in their presence apparently as a result of the increase in the triplet repulsion between X and Y.

9. The presence of bulky groups next to the reaction centre. These groups exert a steric effect, increasing E_{e0} .

10. The solvent polarity. The solvation effect is manifested in a polar solvent if both reactants incorporate polar groups.

Some of the factors enumerated, which influence the activation energy, were not examined previously. They include the force constants of the reacting bonds, the electronegativities of the fragments X and Y, the radii of the atoms X and Y, and the presence of a π -bond next to the reaction centre. The parameters found from experimental data may be used to estimate the activation energy and the rate constants of radical abstraction reactions. The existence of correlation equations for E_{e0} or r_e makes it possible to estimate these parameters for new classes of reactions which have not yet been investigated. The bond dissociation energies can also be calculated from kinetic data with the aid of the IP and MPC methods. Overall, the models described above constitute an effective instrument for the analysis of kinetic parameters of radical reactions.

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The influence of the nature of the chemical reaction on the structure and properties of blends in the reactive blending of polymers

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Abstract. Polymer blends, the preparation of which is accompanied by various chemical reactions and the formation of specific intermolecular bonds between the components, are analysed. The factors influencing the phase structure of the materials obtained are identified and their relative contributions to its formation are estimated. The influence of the blend composition, nature, and concentration of the functional groups and of the temperature regimes in the blending process is examined. A systematic treatment of the results of experimental and theoretical studies of the method of utilisation of functional groups — direct interaction of the reaction groups in the blended polymers or the introduction of low- and high-molecular reagents capable of interacting with the macromolecules of the blend components — is proposed. It is noted that quantitative data on the variation of the thermodynamic affinity of the blend components and on the rates of mass transfer controlling the formation of the phase structure are limited. Certain theoretical models of the structure of reactive polymer blends, which explain their mechanical properties, are discussed. The priority aspects of studies on the processes involved in the reactive blending of polymers are noted. The bibliography includes 212 references.

I. Introduction

The use of polymeric materials in industry has been expanding and the requirements which they must meet have become more stringent. Special interest has been shown in multicomponent blends and alloys. The creation of such polymer systems entails the potential possibility of combining the attractive qualities of each component of the polymer blend in a single material.^{1–5} Much attention has been devoted in recent years to the processes involved in the preparation of polymeric materials by blending components in which chemical reactions take place. Such blending is called reactive.³

The increased attention to reactive blending processes has been induced by the fact that only a few polymers are fully thermodynamically compatible and produce blends which are homogeneous at the molecular level.⁶ The majority of polymers

exhibit limited compatibility and their blends possess a heterogeneous morphology. Practice has shown that, precisely as a consequence of the multiphase nature of multicomponent polymer systems, the materials based on them frequently possess unique performance characteristics, for example an increased resistance to impact loads and optimum stress-strain properties. The chemical nature of the disperse phase and of the dispersion medium as well as the parameters of the phase structure, namely the volume phase ratio, the size and size distribution of the particles of the disperse phase, the degree of dispersion and the coherence of the disperse phase, and interfacial adhesion, are of primary importance in the generation of useful properties.^{7–9} The blend composition and viscoelastic properties of individual components and the conditions in the blending process determine the parameters of the phase structure and the resistance of the blends to coalescence.^{10, 11}

It follows from the fundamental relations describing the thermodynamic equilibrium in disperse systems¹² that the most effective factor which makes it possible to regulate the parameters of the phase structure is the thermodynamic affinity of the components. A low thermodynamic affinity leads to a high interfacial tension and hinders the dispersion of the components on mixing in the melt. In its turn, this leads to a low interfacial adhesion in the solid state and is responsible for the premature mechanical fracture of the material.^{8, 9} Within the framework of traditional approaches (specific selection of the chemical nature of the components, the composition of the blends, and the processing temperature, as well as the introduction of low-molecular or polymeric additives), the compatibilisation problems — the improvement of thermodynamic compatibility and the regulation of the parameters of the phase structure and of its influence on the physicomaterial characteristics of polymer blend — have been investigated fairly completely.^{13–27}

Since the end of the 1980s, reactive blending, in which physical and/or chemical interactions between the molecules of unlike blend components may occur together with blending processes (in the melt or in solution), has attracted increasing attention. The occurrence of exothermic (as a rule) processes, specific intermolecular or chemical interactions — is accompanied by a decrease in the entropy component and an appreciable decrease in the enthalpy component of the free energy. As a result of the decrease in the free energy of mixing (dispersion), the possibilities for the regulation of the phase structure parameters of multicomponent polymeric materials are expanded.

An increase in the thermodynamic affinity of two polymers may be achieved if interchain exchange reactions (mainly transesterification) take place during the blending process or certain

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specific intermolecular interactions occur,^{28,29} such as connecting as a result of the formation of hydrogen bonds,³⁰ ion–dipole and dipole–dipole interactions,³¹ acid–base and ion–ion interactions,³² the formation of π – π complexes,³³ and the formation of molecular charge-transfer complexes.^{34,35} In a number of instances, the decrease in the free energy of mixing (dispersion) is achieved as a result of the increase in its entropy component due to intramolecular repulsion effects.^{36,37}

The reviews of theoretical and experimental studies on compatibilisation,^{38–40} reactive extrusion,⁴¹ and reactive blending of polymers,^{6,42,43} attempts were made to interpret and classify the processes involved in the reactive blending of polymers. The number of experimental studies in the field of the reactive blending of polymers has been increasing, which necessitates a further systematic treatment and classification of the studies in this field.

A classification of multiphase reactive polymer blends with allowance for the differences in the way that reactive blending is carried out is proposed in the present review.

Group A. Reactive polymer blends capable of forming strong physical or chemical bonds between macromolecules under the conditions of thermal and mechanical influences and on specific catalysis. Polymer blends, one of which has been subjected to a preliminary chemical modification in order to introduce functional groups capable of reacting with the macromolecules of the other polymer under the blending conditions, may be assigned to the same group.

Group B. Reactive blends obtained as a result of the introduction of a third high-molecular component capable of reacting with at least one of the main components of the polymer blend to form compatibilising copolymers.

Group C. Reactive blends formed following the introduction of low-molecular components promoting intermolecular and/or intramolecular cross-linking (dynamic vulcanisation) of the phases.

A wide class of blends, formed on blending a linear or network polymer with a monomer or oligomer and subsequent chemical solidification (polymerisation, polycondensation), can also be assigned to reactive polymer systems. These are the so called partial (or complete) interpenetrating polymer networks in which the stages involving the blending of the components and their chemical reaction are as a rule separated. Such attention has been devoted in the literature^{44–47} to the study of the structures and properties of various types of interpenetrating polymer networks and we shall therefore not consider them here.

II. The influence of interchain exchange and of specific interactions in binary polymer blends (group A)

Reactive blending processes may be carried out in solution, in the melt, and in the solid phase. In the solid phase, such processes occur as a result of an external mechanical action, leading to nonelastic deformations and plastic flow. The results of studies on the mechanisms and rates of solid-phase chemical reactions at a high pressure in combination with shear deformation have been examined in detail in a number of communications^{48–51} and are outside the scope of the present review.

Examples of the preparation of group A reactive polymer blends in solution are presented in Table 1. The initial polymers are usually blended in a common solvent and the blends are then precipitated and treated in a specific temperature–time regime. Under such conditions, the most typical interchain exchange reaction for polyesters is transesterification, *i.e.* transesterification of high-molecular polyesters, leading to the formation of the corresponding block copolymers. Hydrolytic chain degradation and chain polycondensation processes occur under these conditions.⁵⁶ According to Fourier-transform infrared spectroscopic (FTIR) data, the transesterification in certain polymer blends at high temperatures may be accompanied also by thermal degrada-

Table 1. Reactive blending of polymers in solution (group A blends).

Polymer 1	Polymer 2	Brief process characteristics	Ref.
PBT	POR	Transesterification	52
	PAr	"	53
PC	PBT	"	54
	PET	"	55
	PETG	"	56
	s-PMMA	"	57
PS	PTCB	Interpolymer Friedel–Crafts reaction	58
PVC	PU	Formation of hydrogen bonds	59
PVP	E–VA	Ditto	60
PVP, POR	PAMA	See ^a	65
POR	Various polyesters	Formation of hydrogen bonds	61
	ENR	Ditto	62
PVC	PCL	Specific intermolecular interactions of unknown nature	63
	Various polyesters	Ditto	64
PC	PPMA	"	66
PVME	SBS	"	67
PA6	PPO	"	68

Note. The following designations have been adopted for the polymers; PBT = poly(butylene terephthalate); POR = phenoxy-resin (bisphenol A polyhydroxyether); PAr = polyarylate (copolyester of bisphenol A and terephthalic and isophthalic acids in proportions of 2:1:1); PC = polycarbonate; PET = poly(ethylene terephthalate); PETG = copolyester of cyclohexane-1,4-dimethanol, ethylene glycol, and terephthalic acid (1:2:3); s-PMMA = syndiotactic poly(methyl methacrylate); PS = polystyrene; PTCB = poly-1,1,2-trichlorobuta-1,3-diene; PVC = poly(vinyl chloride); PU = polyurethane; PVP = poly-4-vinylphenol; E–VA = ethylene–vinyl acetate copolymer; PAMA = poly(alkyl methacrylates); ENR = epoxidised natural rubber; PCL = poly- ϵ -caprolactone; PPMA = poly(phenyl methacrylate); PVME = poly(vinyl methyl ether); SBS = styrene–butadiene–styrene copolymer; PA6 = polyamide 6; PPO = poly(propylene oxide).

^a According to Chong and Goh,⁶⁵ the nature of the intermolecular interaction has not been established in this case.

tion with recombination of macromolecular free radicals, which leads to the formation of graft copolymers.⁵⁷ The formation of an interpolymer microgel in a study of the Friedel–Crafts reaction occurring under mild conditions in a blend of two virtually incompatible polymers has been established.⁵⁸ According to a number of investigators,^{52–58} the compatibilisation of polymer blends is due to the formation of copolymers or interpolymers.

The compatibilisation of polymer blends is also promoted by the formation of hydrogen bonds between the blend components^{59–62} (Table 1). Signs of intermolecular association and of the formation of molecular complexes as a result of strong hydrogen bonding have been observed by high-resolution ¹³C NMR and differential scanning calorimetry in model blends of low-molecular poly(ethylene oxide) and resorcinol, which have two eutectic points on the phase diagram.⁶⁹ The compatibilisation of blends of diethyl maleate-modified ethylene–propylene rubber with polystyrene and with poly(vinyl chloride),⁷⁰ of polyamide 6 with the Mn salt of sulfonated polystyrene⁷¹ and alkaline (Li and Na) ionomers of sulfonated polystyrene,⁷² and also of the styrene–4-vinylpyridine block copolymer with the Zn salt of a carboxylated ethylene–methacrylate copolymer⁷³ is due to the formation of polymeric complexes. Examples of the compatibilisation of polymer blends as a result of specific interactions^{63–68} can also be found in Table 1. The dependence of the intensity of

the intermolecular interactions on the blend composition has been demonstrated.⁷⁴

For ecological reasons, reactive blending has been carried out recently with increasing frequency in polymer melts (in the absence of a solvent). Batch mixers and continuous screw extruders are used as the reactors. Studies on a series of model reactions in solution and in homogeneous melts have shown⁷⁵ that the mechanisms and kinetics of the reactions are virtually analogous in both homogeneous media, provided that diffusion is not the limiting factor. However, as a rule, reactive blending processes are carried out in heterogeneous melts. Interchain block or graft copolymers may then be formed in different proportions (*via* new covalent or ionic bonds). Such *in situ* compatibilisers have molecular segments chemically identical with the segments in the corresponding unreacted homopolymers. The compatibiliser segments are distributed predominantly at the interface, which entails a decrease in interfacial tension and adhesion is strengthened.⁶

The heterogeneous nature of the reactive polymer system predetermines the characteristic features of the kinetics of the chemical reaction. It has been shown in relation to the transesterification reaction in the ethylene–methyl acrylate copolymer/monohydroxylated polystyrene system^{75, 76} that the degree of conversion decreases appreciably with increase in the molecular mass of the monohydroxylated polystyrene. The graft copolymer formed at the interfaces promotes an increase in interfacial adhesion and the stabilisation of the morphology. However, its accumulation at the interface greatly reduces the overall reactivity of the system. The intensity of mechanical mixing becomes a very important factor for the given reaction, since it influences the depth of diffusion and the formation of new interfaces. A marked effect due to the introduction of small amounts of the solvent is also observed: the addition of 1 mass %–2 mass % of 1,2,4-trichlorobenzene or *n*-hexane to the melt of the ethylene–methyl acrylate copolymer/monohydroxylated polystyrene blend greatly increases the overall degree of conversion. According to the authors,^{75, 76} this effect can be accounted for by the increase in compatibility, the improvement in interfacial mixing, and the mutual diffusion in the presence of a solvent. Unfortunately, the relationship between the reaction kinetics and the phase structure of the blend as well as the operating characteristics of the material obtained had not been established in the above investigations. On the whole, information about the diffusional mobility, mutual solubility of the components, the area of interfacial contact, the concentration profiles of the reactants in the interfacial region, as well as the nature of their time variation is needed for the interpretation of kinetic data in heterogeneous reactive polymer systems.^{75, 76}

The conclusions reached in the above studies^{75, 76} agree well with the results of the investigation of transesterification in polyester blends,⁷⁷ for which the influence of the compatibility of the initial components, blending conditions (temperature, duration, and intensity of blending), the ratio of the viscosities of the components, and the presence of catalysts^{78, 79} or inhibitors⁸⁰ in the system on the rate of transesterification has been established. It has also been shown⁸¹ that, in the course of the transreaction, the viscosity of the melt changes; the viscosity increases until both components of the reactive blend have fully reacted.

Transesterification is most often employed in the preparation of group A reactive blends in the melt. An improvement of the compatibility of the components in the melt has been achieved in blends of polycarbonate with poly(butylene terephthalate),^{82–85} poly(ethylene terephthalate),^{78, 79, 86} polyarylate (the copolyester of bisphenol A and terephthalic and isophthalic acids in proportions of 2:1:1),^{87, 88} the copolyester based on cyclohexane-1,4-dimethanol and terephthalic and isophthalic acids (Kodar A150),⁸⁹ a thermotropic polyester consisting of the copolymer of 4,4'-dihydroxybiphenyl and terephthalic and isophthalic acids (Ultrax KB4002),⁹⁰ and polyamide 6.^{91, 92} The transesterification reaction is known to proceed at an appreciable rate at temperatures above 200 °C.⁷⁷ Below this temperature, the rate of

reaction falls and at higher temperatures the Kolbe rearrangement involving the carbonate groups and the pyrolysis of the ester groups makes a significant contribution.⁹³ In a number of instances, the cross-linking and degradation reactions have also been observed, for example in polyacrylamide–chloroprene rubber⁹⁴ and polyacrylic acid–epoxidised natural rubber⁹⁵ blends.

Under the conditions of intense shear blending of incompatible polymers, interchain reactions were noted, as a result of which various copolymers compatibilising the system appeared. Maxwell and Jasso⁹⁶ observed the formation of a three-dimensional network of 'intertwined' homopolymeric stands on blending poly(methyl methacrylate) with polyethylene in an elastic-melt extruder. Under analogous conditions in the blending of polypropylene with high-density polyethylene in the melt, a block copolymer (formed as a result of the cross reactions of the macroradicals), responsible for the improvement of the compatibility of the system components, appears in the blend melt together with the homopolymers.⁹⁷

The series of studies by Santra and coworkers,^{98–101} indicating unlimited mutual solubility in the melt comprising polydimethylsiloxane rubber modified by the inclusion of vinyl groups and the ethylene–methyl acrylate copolymer, is by no means unique. The unlimited mutual solubility is due to the chemical reaction between the vinyl groups at the silicon atoms in the polydimethylsiloxane chains of the rubber with the α -methine groups of the methyl acrylate fragment of the copolymer.^{98, 99} According to the results of dynamic mechanical analysis, for all blend compositions there is a positive deviation of the single glass-transition temperature from the values calculated by Fox's equation.⁹⁸ Synergistic effects have also been observed for the given system in the study of mechanical characteristics,⁹⁹ thermal stability,¹⁰⁰ and rheological properties.¹⁰¹

The improvement of compatibility in reactive blending in the melt may be achieved also as a result of specific interactions, for example the formation of hydrogen bonds between the functional groups of the blend components, as in the poly(ethylene terephthalate)/poly(ether imide) (Ultem 1000),^{102, 103} poly(ethylene terephthalate)/polyurethane, and poly(butylene terephthalate)/polyurethane¹⁰⁴ systems.

The possibilities for compatibilisation and the range of polymeric objects used in reactive blending processes are greatly expanded if one or both components are subjected to a preliminary chemical modification. The aim of the chemical modification in this instance is the introduction into the macromolecules of functional groups capable of reacting under the blending conditions with formation of graft copolymers compatibilising the system. Table 2 presents the blending processes in which one of the components is subjected to preliminary chemical modification. An example of blends with preliminary chemical modification of both components is that of blends comprising 3-mercaptopropyltrimethylsilano-grafted poly(vinyl chlorides) and chlorinated polyethylene in which compatibilisation as a result of the mutual cross-linking of the components was observed.¹³¹ The results of rheological studies, FTIR, and dynamic mechanical analysis of a blend of polypropylene modified by maleic anhydride with the Zn salt of the sulfonated ethylene–propylene–diene monomer have also demonstrated an improved mutual solubility compared with the unmodified polypropylene/ethylene–propylene–diene monomer blends as a consequence of the compatibilisation of the system *in situ*.¹³²

In order to create nucleophilic or base-functionalised polymers for reactive blending with various electrophilic polymers, graft copolymers of olefins, in particular linear low-density polyethylene, with a tertiary amine—2-methylaminoethyl methacrylate (DMAEMA)¹³³—or a secondary amine—*tert*-butylaminoethyl methacrylate (TBAEMA)¹³⁴—have been successfully synthesised. Model studies have demonstrated¹³⁵ that secondary amino-groups can form both ionic and covalent bonds, whereas only ionic bonds or polar interactions with polymers

Table 2. Reactive blending processes in the melt with participation of chemically modified polymers (group A blends).

Polymer 1	Polymer 2 (modified)	Brief process characteristics	Ref.	Polymer 1	Polymer 2 (modified)	Brief process characteristics	Ref.
PA6	PP-g-MAn	Compatibilisation <i>in situ</i> by the graft copolymer formed as a result of the reaction of the anhydride (carboxy-group) and an amine	105–107	S-MAn	LLDPE-g-TBAEMA	Formation of a graft copolymer <i>in situ</i> as a result of reactions leading to the formation of both ionic and covalent bonds	125
	PP-g-AA	Ditto	107		EPR-g-pA	Formation of graft copolymer <i>in situ</i> as a result of the reaction of the anhydride and the amine	126
	EPR-g-MAn	"	108–110				
	EPR-g-AnSA	"	111				
	EPDM-g-MAn	"	112				
	E-MAA	"	113				
	E-AEs-MAn	"	114	MMA-	LLDPE-g-	Formation of graft copolymer <i>in situ</i> as a result of reactions leading to the formation of both ionic and covalent bonds	127
	S-EP-S-g-MAn	"	115	-MAA	-TBAEMA		
	PS-g-MAn	"	116				
	PE-g-MAn	"	117				
	POLDPE	"	118				
PA66	PP-g-MAn	"	119				
	S-EP-S-g-MAn	"	115				
PBT	PP-g-GMA	"	120, 121	PBT	E-AEs-GMA	Ditto	114
E-AA	OPS	Formation of graft copolymer <i>in situ</i> (emulsifying effect)	122	EPDM	PAr-g-BCB	Cyclisation reaction ^a	128
				E-MA	HPS	Transesterification	129
				HDPE	ZSEPTR	Improvement of compatibility as a result of specific intermolecular interactions	130
PVC	LLDPE-g-MAn	Miscibility based on specific intermolecular interactions	123				
S-MAn	LLDPE-g-DMAEMA	Improvement of compatibility as a result of the formation of ionic bonds (polar interactions)	124				

Note. The following designations have been for the polymers: PP-g-MAn = polypropylene modified by maleic anhydride; PP-g-AA = polypropylene modified by acrylic acid; EPR-g-MAn = ethylene-propylene rubber modified by maleic anhydride; EPR-g-AnSA = ethylene-propylene rubber modified by the anhydride of succinic acid; EPDM-g-MAn = ethylene-propylene-diene monomer modified by maleic anhydride; E-MAA = ethylene-methacrylic acid copolymer; E-AEs-MAn = ethylene-acrylic ester-maleic anhydride terpolymer; S-EP-S-g-MAn = styrene-(ethylene-propylene)-styrene triblock copolymer modified by maleic anhydride; PS-g-MAn = polystyrene modified by maleic anhydride; PE-g-MAn = polyethylene modified by maleic anhydride; POLDPE = photooxidised low-density polyethylene; PA66 = polyamide 66; PP-g-GMA = polypropylene modified by glycidyl methacrylate; E-AA = ethylene-acrylic acid copolymer; OPS = oxazoline-modified polystyrene; LLDPE-g-MAn = linear low-density polyethylene modified by maleic anhydride; S-MAn = styrene-maleic anhydride copolymer; LLDPE-g-DMAEMA = linear low-density polyethylene modified by dimethylaminoethyl methacrylate; LLDPE-g-TBAEMA = linear low-density polyethylene modified by *tert*-butylaminoethyl methacrylate; EPR-g-pA = ethylene-propylene rubber modified by a primary amine; MMA-MAA = methyl methacrylate-methacrylic acid copolymer; E-AEs-GMA = ethylene-acrylic ester-glycidyl methacrylate terpolymer; EPDM = ethylene-propylene-diene monomer; PAr-g-BCB = polyarylate based on bisphenol A and terephthalic and isophthalic acids (2 : 1 : 1) modified by 1,2-dihydro-4-chloroformylbenzocyclobutene; E-MA = ethylene-methyl acrylate copolymer; HPS = monohydroxylated polystyrene; HDPE = high-density polyethylene; ZSEPDM = Zn salt of sulfonated ethylene-propylene-diene monomer.

^a Thermally reversible cyclisation reaction between the unsaturated side bonds of EPDM and the *o*-quinondimethane end groups of PAr-g-BCB.

containing carboxy- or maleic anhydride groups are characteristic of tertiary amino-groups. The reactive blending of linear low-density polyethylene, chemically modified by DMAEMA, with the styrene-maleic anhydride copolymer in the melt ensures an improved compatibility of the components. This conclusion was reached on the basis of electron microscope data and was accounted for by the strong specific polar interactions between the acid anhydride and the basic amino-groups. However, the improvement of the mechanical properties of these reactive blends proved to be slight.^{124, 125} It was also established that the secondary amino-group in TBAEMA is more reactive in relation to the carboxy- or anhydride groups than the primary or tertiary amino-groups. A decrease in the size of the particles of the disperse phase, accompanied by an increase in the tensile strength σ_b , the relative tensile elongation at break ϵ_b , and the breaking energy on impact

by 20%–50% compared with the nonreactive linear low-density polyethylene/styrene-maleic anhydride blends was observed under these conditions in systems comprising linear low-density polyethylene modified chemically by TBAEMA and the styrene-maleic anhydride copolymer.¹²⁵

A more significant increase in the stress-strain characteristics has been observed in the reactive blends of linear low-density polyethylene modified chemically by TBAEMA with the methyl methacrylate-methacrylic acid copolymer (by 500%–800%) compared with the nonreactive linear low-density polyethylene chemically modified by TBAEMA/poly(methyl methacrylate) blends.¹²⁷ Three macromolecular reactions take place in blends of linear low-density polyethylene modified chemically by TBAEMA and the methyl methacrylate-methacrylic acid copolymer: the formation of the amide, the formation of the

carboxylate anion, and the formation of the imide ring as a result of the interactions of two neighbouring carboxy- and carboxylate groups of the copolymer with the amino-group of the linear low-density polyethylene modified chemically by TBAEMA with elimination of isobutene and an alcohol.^{127, 135, 136} The last reaction leads to the formation of a graft copolymer, which increases interfacial adhesion and hence greatly improves the stress-strain characteristics of the reactive blends.

As can be seen from the relation presented in Fig. 1, the values of U_t for the reactive blends containing more than 50 mass % of the linear low-density polyethylene modified chemically by TBAEMA exceeded the additive values ('positive' effect¹³⁷). For plastics with improved (as a result of the inclusion of rubber particles in the brittle polymer matrix) impact strength, such effects have been frequently observed.^{1, 7, 10} Among the polymer blends consisting of a ductile (plastic) matrix and a brittle disperse phase, only very few exhibit 'positive' effects [for example, the polycarbonate/poly(methyl methacrylate) and polycarbonate/styrene-acrylonitrile copolymer systems].¹³⁷ Within the framework of the 'cold drawing' concept,¹³⁸ the absorption of impact energy in these systems can be explained by the plastic deformation of the brittle disperse phase. The reason for such deformation is the high compressive stress arising on bulk-phase deformation of a two-phase system by the tensile stress in the equatorial planes of spheres dispersed in a matrix and caused by the difference between the Young's moduli and the Poisson coefficients of the disperse spherical phase and the matrix. According to Liu *et al.*,¹²⁷ the 'positive' effect in the compatibilised linear low-density polyethylene chemically modified by the TBAEMA/methyl methacrylate-methacrylic acid copolymer blend can be explained by a brittle-to-ductile transition in the disperse phase. According to electron microscope data, such blends are characterised by a more finely disperse and inhomogeneous morphology than nonreactive linear low-density polyethylene chemically modified by TBAEMA/poly(methyl methacrylate)-methacrylic acid copolymer blends. The particles of the methyl methacrylate-methacrylic acid copolymer are anchored to a matrix comprising the linear low-density polyethylene modified chemically by TBAEMA with the aid of fibril-like elements, which appear as a result of the drawing of such polyethylene during impact fracture and indicate very strong adhesion between the phases.

The strong interfacial adhesion in the systems obtained by reactive blending has been confirmed by the results of the analysis of the concentration dependence of the elastic modulus E within

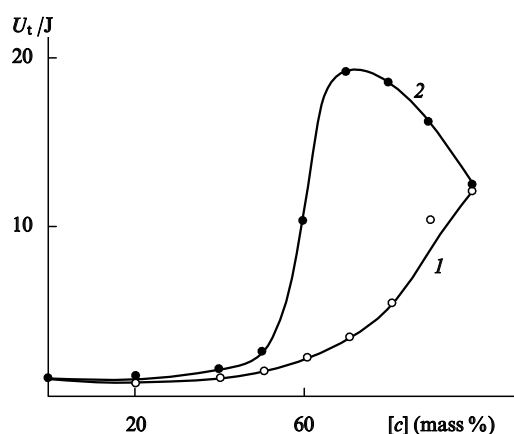


Figure 1. The influence of blend composition on the total absorbed impact energy U_t for nonreactive linear low-density polyethylene chemically modified by TBAEMA/poly(methyl methacrylate) blends (1) and reactive linear low-density polyethylene chemically modified by TBAEMA/methyl methacrylate-methacrylic acid copolymer blends (2);¹²⁷ [c] — content of the linear polyethylene modified chemically by TBAEMA.

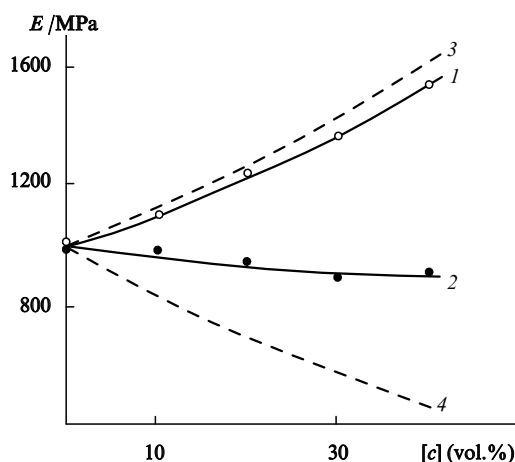


Figure 2. Experimental (1, 2) and theoretical (3, 4) dependences of Young's modulus on the volume fraction of the poly(methyl methacrylate) disperse phase for nonreactive linear low-density polyethylene chemically modified by TBAEMA/poly(methyl methacrylate) blends (2, 4) and reactive linear low-density polyethylene chemically modified by TBAEMA/methyl methacrylate-methacrylic acid copolymer blends (1, 3);¹²⁷ [c] — content of the methyl methacrylate-methacrylic acid copolymer [or poly(methyl methacrylate)].

the framework of Takayanagi's adhesion theory.¹³⁹ As can be seen from Fig. 2, the experimental data for the linear low-density polyethylene modified chemically by TBAEMA/methyl methacrylate-methacrylic acid copolymer reactive blends (curve 1) virtually coincide with data calculated in accordance with the 'perfect adhesion' model (curve 3). For the nonreactive linear low-density polyethylene modified chemically by TBAEMA/poly(methyl methacrylate) blends, the experimental Young's moduli (curve 2) lie appreciably below the 'ideal adhesion' line but appreciably above the 'loose inclusions' line (curve 4). According to Liu *et al.*,¹²⁷ the transfer of stress between the phases in the given nonreactive system takes place by virtue of a mechanical interfacial contact arising on cooling the mixture, because the matrix comprising linear low-density polyethylene modified chemically by TBAEMA crystallises after the solidification of the poly(methyl methacrylate) phase inclusions and may compress them.

Cross reactions of various types always occur in the blending of polymers in melts: chain transfer by the radical degradation products and subsequent recombination of the macroradicals, chain transfer with rupture as a result of molecular and ionic reactions, and cohydrolysis and transesterification reactions. Deliberate employment of these reactions may exert a favourable influence on the morphology and properties of polymer systems.

III. Reactive blending in multicomponent polymer systems with participation of high-molecular compatibilisers (group B)

The introduction of a third high-molecular component may serve as one of the methods for the compatibilisation of blends of two incompatible polymers. Polymeric compatibilisers, consisting of reactive copolymers or chemically modified polymers of type X-Z (where Z is a long-chain reactive segment or functional group attached to the main chain), may compatibilise the polymer pair X and Y subject to the condition that Z is capable of reacting chemically with the polymer Y. Table 3 presents certain examples of systems of this kind investigated in recent years (the studies published up to 1990 have been examined in another review⁶). The chemical nature and structure of the component X and of the unreactive segment of the polymeric compatibiliser frequently differ, but the latter is nevertheless capable of specific interactions

Table 3. Processes involving compatibilisation by means of reactive copolymers or chemically modified polymers introduced separately (group B blends).

Compatibilising blend	Polymeric compatibiliser	Ref.
PA6/ABS	Various S-AN and S-MAN	140
PA6/PS	PS-g-TAN or S-MAN	141
PA6/PS	S-MAA Na-ionomer	142
PA6/S-AN	S-MAN	143
PA6/S-AN	MAN- or oxazoline-grafted styrene copolymers	144
PA6/HNBR ^a	Chemically modified nitrile rubbers in the presence of cross-linking agent	145
PA6/PP (or HDPE)	E-MAA-ICA	146
PA6/PP	PP-g-MAN	105, 147
PA6/PP	PP-g-AA	148
PA6/PP	Peroxide emulsifiers	149
PA6 (or PA6,6)/PP	(1) PP/E blend (2) PP-g-MAN	150–152
PA6,6/PP	PP-g-MAN	153
LCP/PP	(1) PP/E blend (2) PP-g-MAN	151, 152 154
LCP(PDMPO/PS)	S-GMA	155
SEPTR/PP	E-MAA Na- and Zn-ionomers	156
NR/HDPE ^a	Liquid NR	157
PDMPO/IPE	S-VP	158
PS/LDPE	PS-g-O-CPE	159
PMMA/S-AN	S-ECA	160

Note. The following designations have been adopted for the polymers: ABS = ternary acrylonitrile–butadiene–styrene copolymer; S-AN = styrene–acrylonitrile copolymer; PS-g-TAN = polystyrene modified by trimellitic anhydride; S-MAA = styrene–methacrylic acid copolymer; HNBR = hydrogenated nitrile rubber; PP = polypropylene; E-MAA-ICA = ethylene (80 mol. %)–methacrylic acid–isobutyl acrylate terpolymer (Surlyn 9020); E = reactive ethylene-based terpolymer (Lotader AX-8660); LCP = liquid-crystal polymer based on 6-hydroxy-2-naphthoic acid (70 mol. %) and *p*-hydroxybenzoic acid (30 mol. %) (Vectra A950); PDMPO = poly(2,6-dimethyl-1,4-phenylene) oxide; S-GMA = styrene–glycidyl methacrylate copolymer; NR = natural rubber; IPE = ionomeric polyethylene [Zn-neutralised ethylene–methacrylic acid copolymer (Surlyn 9730)]; S-VP = styrene-4-vinylpyridine block copolymer; LDPE = low-density polyethylene; PS-g-O-CPE = polystyrene (modified by oxazoline)-carboxylated polyethylene graft copolymer; PMMA = poly(methyl methacrylate); S-ECA = styrene–ethyl 2-cyanoacrylate copolymer.

^a In this cases cross-linking reactions take place together with the interfacial reactions during the blending process.

leading to an increase in the thermodynamic affinity of the components. It is noteworthy that a considerable proportion of ternary polymer systems (Table 3) may be obtained from binary blends (Table 2) by ‘dilution’ with an unmodified basic polymer (for example, polyamide/polyolefin modified by maleic anhydride/polyolefin).

In the majority of reactive blends of this category, a polyamide (polyamide 6 or polyamide 66) is used as a component which may react with compatibilisers containing the anhydride or carboxy-functional groups^{105, 140–153} with formation of amide or imide bonds. Other examples of this kind are the inclusion of either the reactive oxazoline group^{159, 161} or the epoxide group. The latter may be present in epoxidised rubber¹⁶² or in the terpolymer based on poly-ε-caprolactone. A different approach to the improvement of compatibility has been described^{156, 158, 163} — as a result of ionic interactions of interchain Na or Zn salts. This method affords rubber-modified blends with an improved impact strength.¹⁶³

The principle of the interaction of reactive groups of diverse polymers capable of forming statistical or block copolymers, acting as compatibilisers in blends, has been used in the blending in a melt of polyamide 6 with various styrene and acrylonitrile copolymers. The compatibilising effect is manifested by styrene–acrylonitrile copolymers containing functional groups of the type of maleic anhydride or oxazoline. In order to regulate the dimensions of the disperse phase of the styrene–acrylonitrile copolymer, an attempt has been made to optimise the composition of the reactive system as regards the type and concentration of the functional groups, the content of the reactive compatibiliser, and its compatibility with the styrene–acrylonitrile copolymer.^{140, 144}

The same principle has been used to improve the compatibility of blends of polyamide 6 and polypropylene by the introduction of acrylic acid-modified polypropylene as the reactive compatibiliser.¹⁴⁸ Together with the strong hydrogen-bonding interactions in such ternary blends, the terminal amino-groups of the polyamide are capable of reacting with the acid groups of the modifier. The influence of the blending conditions in the extruder (temperature, rate, the moment of rotation during blending, the presence of a vacuum, *etc.*) on the strength properties and morphology of the blends has been described. The formation of a graft copolymer on introduction of a polymeric compatibiliser has been demonstrated by IR spectroscopy.

Even a small amount of the compatibiliser may alter significantly the structure of the polymer blend. It has been shown¹⁴⁷ that maleic anhydride-modified polypropylene, introduced at a concentration up to 1.5 mass %, can fully alter the kinetics of the crystallisation and the crystalline structure of the polypropylene/polyamide 6 blend. The crystallisation of polyamide 6 is almost fully suppressed at its usual crystallisation temperature and virtually complete so called retarded (or concerted) crystallisation of polyamide 6 and polypropylene takes place. This effect had been observed earlier in noncompatibilised blend systems such as polyamide 6/poly(vinylidene fluoride), poly(butylene terephthalate)/poly(vinylidene fluoride), and polyethylene/polyoxymethylene¹⁶⁴ and also in compatibilised blends.¹⁵⁰ It has been suggested that this effect is a consequence of the dilution of the polyamide phase by the polypropylene–polyamide 6 graft copolymer.¹⁴⁷

Blends of poly(2,6-dimethyl-1,4-phenylene) oxide with Surlyn 9730 ionomeric polyethylene, which is a Zn-neutralised statistical ethylene–methacrylic acid copolymer, constitute an example of compatibilisation as a result of specific interaction in ternary polymer/polymer/polymeric compatibiliser systems.¹⁵⁸ The styrene–4-vinylpyridine block copolymer with a ratio of the styrene and vinylpyridine blocks of 59/41 was used as the compatibiliser. According to differential scanning calorimetric data, the styrene and vinylpyridine blocks of this copolymer interact with the poly(2,6-dimethyl-1,4-phenylene) oxide and ionomeric polyethylene phases respectively. According to the results of FTIR studies, the specific interaction between the vinylpyridine blocks of the compatibiliser and the ionic groups of the ionomeric polyethylene is of the ion–dipole type. The results of mechanical tests (Fig. 3) have shown that the introduction of the styrene–4-vinylpyridine block copolymer increases the values of *E* and σ_b over the entire range of compositions. The values of ϵ_b vary in parallel with increase in the content of the compatibiliser in blends enriched in poly(2,6-dimethyl-1,4-phenylene) oxide and the variation is anti-parallel in blends enriched in the ionomeric polyethylene. According to Jo *et al.*,¹⁵⁸ these results are a consequence of the increase in the degree of dispersion of the polymeric filler and the adhesion between the poly(2,6-dimethyl-1,4-phenylene) oxide and ionomeric polyethylene phases. The fractograms, obtained by scanning electron microscopy, of the blend specimens after tensile tests confirm the improvement of the interfacial adhesion in the presence of the block copolymer: in the absence of the styrene–4-vinylpyridine block copolymer, the spherical particles of the disperse phase [poly(2,6-dimethyl-1,4-phenylene) oxide] separate from the matrix owing to the weak transfer of stresses and deformations, while in the presence of the styrene–4-vinylpyr-

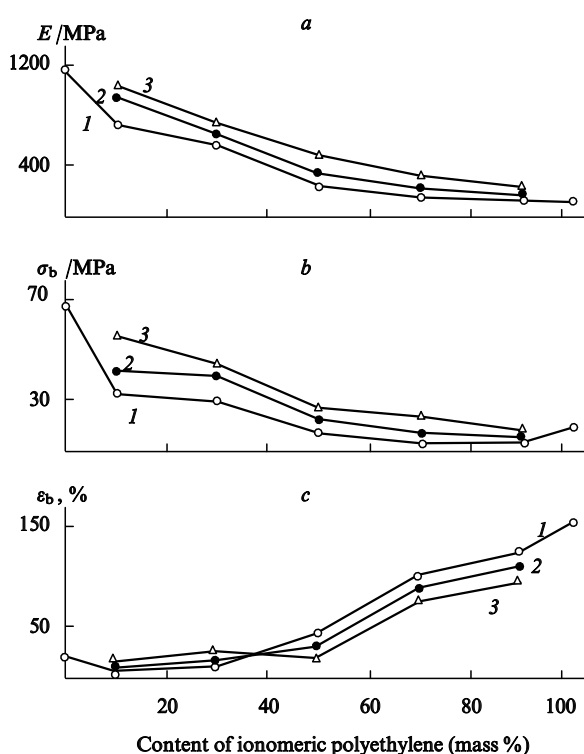


Figure 3. The influence of the introduction of the styrene-4-vinylpyridine block copolymer on the elastic modulus E (a), the tensile strength σ_b (b), and the relative elongation at break ε_b (c) for poly(2,6-dimethyl-1,4-phenylene) oxide/ionomeric polyethylenes of different composition blends.¹⁵⁸ Content of the styrene-4-vinylpyridine block copolymer (mass %): (1) 0; (2) 5; (3) 10.

idine block copolymer the disperse phase is deformed and elongated, as a result of which it is anchored more strongly to the matrix. The specific interaction between 4-vinylpyridine and the transition metal cation has been used also for the compatibilisation of blends comprising rubbers and amorphous polymers, for example the sulfonated polystyrene/ethyl acrylate-4-vinylpyridine copolymer,¹⁶⁵ the sulfonated ethylene-propylene-diene monomer/styrene-4-vinylpyridine block copolymer,¹⁶⁶ and the Cu-neutralised carboxylated polybutadiene/styrene-4-vinylpyridine block copolymer¹⁶⁷ blends.

IV. Reactive blending with participation of low-molecular compounds. Dynamic vulcanisation (group C)

A promising approach to the compatibilisation of polymer blends is the introduction of reactive low-molecular compounds which tend to form covalent bonds with one or both blend components and promote the formation reactions of statistical, block, or graft copolymers, linear or branched (compatibilisation mechanism I), cross-linked in one of the coexisting phases (compatibilisation mechanism II), or cross-linked in both polymer phases (compatibilisation mechanism III). Small amounts (0.1 mass %–3.0 mass %) of added low-molecular compounds are usually employed. This constitutes their main economic advantage over polymeric compatibilisers, which, apart from the expense and complexity of their synthesis, are as a rule effective at higher concentrations.

Examples of the formation of group C reactive blends are presented in Table 4. The compatibilisation mechanism I involves the formation of compatibilising copolymers under the influence of catalytic and noncatalytic interchain reactions. Toluene-*p*-sulfonic acid or phosphites catalyse transamidation reactions in

Table 4. Compatibilisation of polymer blends with participation of reactive low-molecular compounds (group C blends).

CM ^a	Compatibilised blend	Low-molecular compound	Ref.
I	PET/PA6,6	Toluene- <i>p</i> -sulfonic acid	168, 169
	PA6/PA6,6	Triphenyl phosphite	169
	LLDPE/S-VBA	Peroxide + coreagent	170
	PVC/PP	Bismaleimide	171
	PBTP/EPDM-g-FA	Oligomers	172
	S-MAN/BBR	Dimethylaminoethanol	173
	PP/PE	Peroxides	174–177
	PVC/PE	Benzoyl peroxide + + TAIC	178
	PVC/E-VA	Benzoyl peroxide + + TAIC	179
	PP (or PA6)/nitrile rubber	Di(hydroxymethyl)phenolic derivatives	180
II	PP/E-VA (or E-MA)	Dibutyl tin oxide	181
	ER/PC	Dicarboxylic acid anhydride	182, 183
	ER/PEI ^b	Di(aminophenyl)sulfone	184
	PI/PAmA ^b	Pyridine + acetic anhydride	185
	PS/SBR	Dicumyl peroxide	186
	PS/EPDM	Lewis acids	187
	PP/EPDM	Peroxide or sulfur cross-linking agents	188–193
	PP/SEPR	Peroxides	194
	PP/PEVP/SEPTR	Dicumyl peroxide	195, 196
	PP/BANR	Bismaleimide and peroxide	197
	PA/BANR	Peroxide or sulfur cross-linking agents	198
	PCL/HNK	<i>p,p'</i> -Dibenzoylquinone dioxime	199
	VDF-HFP/nitrile rubber (or ECHR)	Triazinedithiol complex	200
	NR/LDPE	Peroxide and coreagents	201
	PP (or PP-g-AA)/PBD (or BNR, SEPR, NR, SBR)	Ditto	202

Note. The following designations have been adopted for the polymers: LLDPE = linear low-density polyethylene; S-VBA = styrene-vinylbenzaldehyde copolymer; EPDM-g-FA = ethylene-propylene-diene monomer modified by fumaric acid; BBR = brominated butyl rubber; TAIC = triallyl isocyanurate; ER = epoxide resin; PEI = poly(ether imide) (Ultem 1000); PI = polyimide; PAmA = poly(amic acid); SBR = styrene-butadiene rubber; EPR = ethylene-propylene rubber; BANR = butadiene-acrylonitrile rubber; VDF-HFP = vinylidene fluoride-hexafluoropropylene copolymer; ECHR = epichlorohydrin rubber; PBD = *cis*-polybuta-1,4-diene; BNR = butadiene-nitrile rubber.

^a Compatibilisation mechanisms (CM): I — formation of copolymers; II — formation of copolymers and cross-linking of one phase; III — formation of copolymers and cross-linking of both phases of the blend.

^b Blending of polymers in solution.

a melt comprising blends containing various polyamides and polyesters.^{168, 169} Free-radical reactions, initiated by peroxides and/or shear, also lead to the formation of compatibilising copolymers as a result of the recombination of the macroradicals formed, in the presence of an additional reagent — the interchain connecting agent (ICA), for example reagents such as bismaleimide.^{170, 171} In blends comprising poly(butylene terephthalate) and a fumaric acid-modified ethylene-propylene-diene copolymer, polyamide oligomers can act as ICA as a consequence of reactions with carboxy-groups.¹⁷² It is noteworthy that Table 4 does not include examples of compatibilising systems containing fillers and reinforcing agents (mica, graphite, talc, calcium carbo-

nate, cellulose, glass fibre, *etc.*). Such systems have been examined in Xanthos' review.²⁰³ Standard organofunctional silanes or titanate and zirconate compounds developed later are widely used as ICA in these systems. In the polypropylene/CaCO₃ systems, sulfonyl azides, having the general formula N₃SO₂-R'-COOH and containing the azide and carboxy-groups, are reactive in relation to both polypropylene and CaCO₃.²⁰⁴

It has been shown¹⁷³ that dimethylaminoethanol forms bonds between brominated butyl rubber and the styrene-maleic anhydride copolymer. Reactive organofunctional titanates compatibilise various polymer systems (for example, polyoxymethylene/polyacrylate²⁰⁵) via catalytic exchange reactions and also via their involvement in other reactions, depending on the type of polymer and the structure of the titanate.

The compatibilisation mechanism II (Table 4) operates in the presence in the blend of a component capable of being cross-linked on treatment with various reagents. It is usually believed^{6,203} that compatibilising copolymers are then formed simultaneously *in situ*. With the exception of plastic/plastic blends, such as polypropylene/polyethylene,¹⁷⁴⁻¹⁷⁷ poly(vinyl chloride)/polyethylene,¹⁷⁸ epoxide resin/polycarbonate,^{182,183} epoxide resin/poly(ether imide) (Ultem 1000),¹⁸⁴ and polyimide/poly(amic acid),¹⁸⁵ all the examples of the compatibilisation mechanism II refer to blends of the plastic/rubber type. These blends are obtained with the aid of the so called 'dynamic vulcanisation', *i.e.* the process involving the cross-linking of only the rubber component on blending in the melt.^{179-181,186-199}

The intercrossed (intercross-linked) rubber/rubber²⁰⁰ and rubber/plastic^{201,202} blends (Table 4) can serve as examples of the compatibilisation mechanism III. It is believed that the phase segregation in these systems is suppressed by the formation of chemical bonds in the interfacial layer. It has been postulated that such morphology occurs in various blends compatibilised by cross-linking, such as styrene-butadiene rubber/butyl rubber, natural rubber/butyl rubber, *etc.*^{1,206} which include components undergoing cross-linking at approximately the same rate. The required properties may be obtained also by reducing the overall rate of cross-linking, which favours interdiffusion and mutual overlapping of the phases.²⁰¹ In the field of study of rubber blends, efforts have been mainly concentrated on the development of common cross-linking agents (such as the triazinedithiol complex²⁰⁰) with comparable rates of vulcanisation and similar solubilities in the blend components.

Among all the variants of the reactive blending of polymers examined, dynamic vulcanisation (DV) has been most fully investigated. The thermoplastic elastomers (TPE) formed on dynamic vulcanisation are rubber materials, which can be processed in the melt like the usual thermoplastic materials but at the operating temperature possess properties analogous to those of a vulcanised elastomer.²⁰⁷ In recent years, there has been a steady growth of interest in these materials, which compete successfully with traditional thermocured rubbers in the market for industrial cured rubber products.^{11,181} The main task is to use of the DV method to create a multicomponent system with particles of the vulcanised elastomer included in a plastic matrix which can be processed in the melt. The rubber components should be vulcanised during its blending with the thermoplastic polymer.

The first compositions of this kind were obtained in the 1960s-1970s.^{208,209} A series of rules governing the appearance of the set of useful properties of materials of the TPE type have now been discovered. The study of dynamically cross-linked compositions based on a large series of rubbers and thermoplastics^{180,196,210} has demonstrated that thermoplastic vulcanisates, in which the surface energies (critical wetting surface tensions) of the plastic and elastomer are similar, the molecular length between the entanglements in the initial elastomer is small, and the plastic has a degree of crystallinity of the order of 15%-30%, possess the most effective stress-strain properties. In relation to the polypropylene/ethylene-propylene-diene mono-

mer system, obtained by the DV method in the presence of a sulfur-containing cross-linking system, it has been shown that the stress-strain behaviour of TPE depends on the particle size of the dispersed rubber, the composition of the blend (Fig. 4), and the density of the cross-links in the elastomer phase (Fig. 5).²¹⁰ It was found that a small number of cross-links [5×10^{-5} mol (ml of elastomer)⁻¹] is needed for a significant improvement of the elastic recovery after drawing. The tensile strength σ_b of the given TPE increases monotonically with increase in the number of cross-links of the elastomer phase, but the compositions remain processable as thermoplastics even for high cross-linking densities, only small changes in the hardness of the compositions being observed following a significant alteration of the degree of vulcanisation.²¹⁰ For the TPE based on polypropylene and the ethylene-propylene-diene monomer (Santoprene 201-73), it has been shown¹⁹⁰ that the elastic recovery is greater, the lower the value of Young's modulus and the higher the yield stress of the matrix polymer (polypropylene).

The dynamic vulcanisation of a component of ethylene-propylene rubber alters radically the structure and properties of the

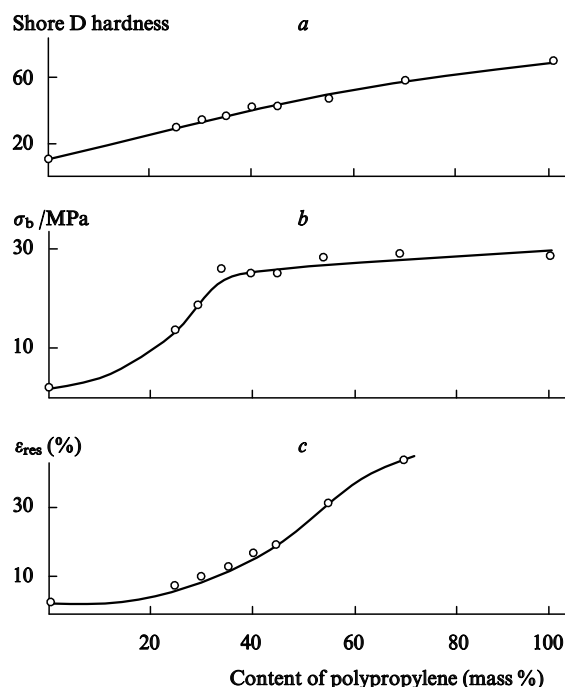


Figure 4. Dependence of the hardness (a), tensile strength (b), and residual deformation (c) on blend composition for dynamically vulcanised TPE based on polypropylene and the ethylene-propylene-diene monomer.²¹⁰

TPE based on polypropylene and ethylene-propylene rubber.^{194,211} The blend containing noncross-linked ethylene-propylene rubber is characterised by the presence of polypropylene domains randomly distributed in the rubber matrix. Dynamic vulcanisation leads to phase inversion, as a result of which the plastic phase (polypropylene) becomes continuous. After crystallisation, its structure resembles a cobweb surrounding the particles of the cross-linked ethylene-propylene rubber. The melting behaviour of the polypropylene phase in nonvulcanised polypropylene/ethylene-propylene rubber blends is independent of the overall blend composition and the molecular mass of the ethylene-propylene rubber. In the presence of the cross-linked rubber component, an appreciable decrease in the effective (observed) melting point of the polypropylene in the blend is observed. The supermolecular structure of the polypropylene phase has been described within the framework of the 'leaf-spring' model, according to which the individual lamellae in the stacks (piles) are linked

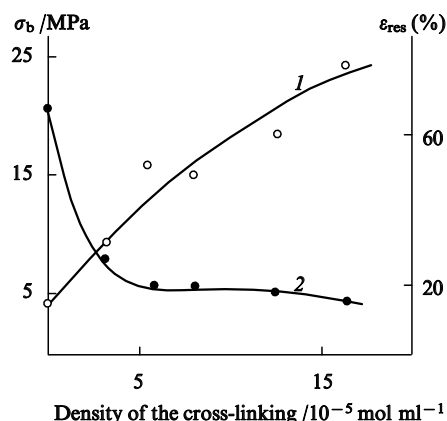


Figure 5. The influence of the density of the cross-linking of the elastomer phase on the tensile strength σ_b (1) and the residual elongation on extension ϵ_{res} (2) for dynamically vulcanised TPE based on the polypropylene/ethylene-propylene-diene monomer blend (40/60).²¹⁰

solely to their upper and lower neighbours in the network of nodes, whilst the regions between lamellae remain unconnected. By virtue of this unusual geometry, this polypropylene with stacked lamellae can undergo almost complete elastic recovery even after appreciable deformation.¹⁹⁴

The formation of covalent bonds between the thermoplastic and rubber phases in the course of the DV process is a decisive factor in the establishment of the stress-strain properties of the TPE. It is seen from the drawing diagram for blends of different polypropylenes and rubbers (Fig. 6) that the values of σ_b for the vulcanised materials are significantly higher than for the non-cross-linked systems (curves 1). Cross-linking systems ensuring the covulcanisation of the polymeric components are preferable for the improvement of the stress-strain characteristics (curves 3). The effectiveness of covulcanisation increases if polypropylene

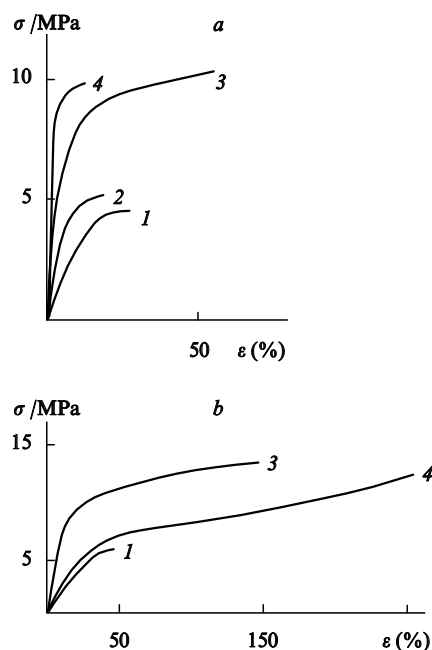


Figure 6. The drawing diagrams for TPE based on polypropylene/brominated butyl rubber (40/60) (a) and polypropylene modified by acrylic acid/butadiene-nitrile rubber containing terminal amino-groups (40/60) (b) blends. TPE: nonvulcanised (1) and vulcanised in the presence of tetramethylthiuram disulfide/sulfur (2), bismaleimide/dicumenyl peroxide (3), and phenolic resin (4) systems.²⁰²

has been subjected to a preliminary chemical modification, for example with acrylic acid (curves 3 and 4 in Fig. 6b). The improving of adhesion between the phases as a result of the formation of covalent bonds reduces the glass transition temperature of the amorphous regions of the polypropylene.²⁰²

Thus, by regulating the nature of the polymer chain of the compatibiliser and the reactivity of the functional groups, it is possible to alter specifically the structure and interaction energy in the interfacial layer. The increase in the cohesion energy in one of the phases as a result of specific cross-linking makes it possible to regulate effectively the degree of dispersion and the physico-mechanical properties of the filler polymer.

V. Conclusion

The development of polymer blends and alloys based on reactive or compatibilised *in situ* polymeric components is one of the fields of study of high-molecular compounds undergoing the most vigorous dynamic development. According to data from various sources, in 1993 the market in compatibilisers and ICA (without modifying agents) was estimated as 10 000–20 000 tonnes annually. It is expected⁴⁰ that by the year 2000 this amount will have increased to 80 000 annually.

The technology for the reactive blending of polymers not only opens the way to new possibilities for the employment of polymeric products already available but also permits the creation of blends the preparation of which has been economically unfavourable. The extensive possibilities of synthetic organic chemistry can be used, in principle, for the preparation by the reactive blending method of diverse high-molecular substances and polymer blends based on a relatively small number of available polymers.^{38, 39, 212}

The store of experimental data accumulated hitherto makes it possible to characterise the past stage in the study of reactive blending processes as empirical. A multiplicity of types of chemical reactions and specific interactions in polymer solutions and melts, acting on the thermodynamic compatibility of components of reactive systems and on the parameters of their phase structure, have been tested and the influence of the blend composition, concentration of functional groups, and the temperature-time blending regimes has been discovered. At the same time, in the vast majority of cases, the relations obtained must be assessed as qualitative. The fundamental conclusion that the thermodynamic affinity of the components improves on reactive blending is usually based on indirect data, such as the decrease in the particle size of the disperse phase and, more rarely, the mutual approach of the glass-transition temperatures of the coexisting polymeric phases. There has been virtually no monitoring of the degree of conversion of the reactive groups, which is of fundamental importance for the establishment of correlations between the component ratio, the concentration and nature of the reactive groups in the initial blends, and the blending regime (temperature, duration, rate, and intensity of mixing), on the one hand, and the parameters of the morphology and phase structure and the physico-mechanical characteristics of the material after the completion of the reactive blending process, on the other.

The construction of a theoretical model which would permit a quantitative prediction of a property of polymeric materials of this kind appears extremely problematical at the present time owing to the deficiency of systematic studies embracing simultaneously the chemical (the nature and kinetics of the reactions) and physico-chemical (diffusion, crystallisation, and phase segregation) aspects of the formation of the structure and the establishment of properties. The kinetic theory of macromolecular reactions in multicomponent heterogeneous solutions and melts of polymer blends in a flow (for example in the extruder or continuous operation mixer), taking into account three-dimensional diffusion and the variation of the phase state of the system during the reaction, is of particular interest. Variation of the ratio of the rates of the chemical reaction, responsible for the variation of the

composition of the reaction system, and of mutual diffusion, which controls the redistribution of the components in the bulk of the coexisting phases and in the interfacial region, opens a path to the regulation of the parameters of the phase structure (including interfacial adhesion) and ultimately of the set of technological and performance characteristics of the polymeric materials obtained by reactive blending.

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The structure, synthesis, and immunomodulating activity of bacterial lipopeptides and their analogues

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Abstract. The current state and prospects for the use of natural lipopeptides and their synthetic analogues in the study of fine mechanisms of functioning of complex biological systems and in the solution of various problems of biochemistry and medicine are considered. The results of investigations related to the synthesis and biological activity of lipopeptides are summarised. The data on the application of lipopeptides as components of synthetic vaccines and antitumour drugs are discussed. The bibliography includes 71 references.

I. Introduction

Lipopeptides are compounds that contain a peptide chain to which one or several fatty acid residues are covalently linked. The molecules of the known lipopeptides comprise from four to sixteen amino acid residues.¹ Natural lipopeptides have been mostly detected in Gram-negative bacteria and Actinomycetes, though they are present also in some species of lower fungi. The majority of lipopeptides are characterised by strict structural specificity as regards the producing organism.

The search for the means directed against bacterial infections has stimulated studies on the structure of various bacteria. Thus, the first systematic studies on the cell wall of mycobacteria were begun in the 1970's.^{2–4} It was established^{4,5} that the fraction exhibiting the highest biological activity contains fragments of peptidoglycans, the minimum structural unit of which is *N*-acetylmuramyl-L-alanyl-D-isoglutamine (muramyl dipeptide, MDP). Later, the attention of numerous research groups was focussed on the study of fragments of natural peptidoglycans and their synthetic derivatives.^{6–9}

These studies have shown that bacterial lipoproteins and their fragments, lipopeptides, possess biological activity. The establishment of immunostimulating and antitumour activities of bacterial lipopeptides was followed by numerous attempts directed at the

synthesis of their analogues. However, the preparation of synthetic lipopeptides involved certain difficulties due to the presence in their structure of aliphatic and peptide fragments as well as the necessity to obtain optically pure compounds.

The biological activity of bacterial lipopeptides was studied in parallel with the analysis of approaches to the synthesis of their analogues. It was established that the synthetic analogues also possess immunostimulating properties and can exhibit pronounced antitumour activity. Owing to these properties, lipopeptides have received particular attention of investigators as potential components of synthetic vaccines and antitumour drugs.

II. The structure of a bacterial cell wall

The backbone of a bacterial wall is built predominantly of a homogeneous polymer, the peptidoglycan (murein). The peptidoglycan is a heteropolymer that consists of chains with alternating residues of *N*-acetylglucosamine and *N*-acetylmuramic acid [3-*O*-(1-carboxyethyl)-*N*-acetyl-D-glucosamine] linked together with β -1,4-glycosidic bonds.¹⁰

These unbranched chains of a heteropolysaccharide muramine form the murein skeleton. The residues of muramic acid are linked to amino acids *via* the carboxy groups of lactic acid with peptide bonds. The typical amino acids of murein are L-alanine, D-glutamic acid, *meso*-diaminopimelic acid (for Gram-negative bacteria) or L-lysine (for Gram-positive bacteria), and D-alanine. The heteropolysaccharide chains are cross-linked by peptide bridges to form a bag-shaped giant molecule, the murein bag, which functions as a backbone of the cell wall.¹⁰

In Gram-negative bacteria, the murein network has only one layer and constitutes less than 10% of the dry mass of the cell wall (in *E. coli*). Murein contains only *meso*-diaminopimelic acid but not lysine; interpeptide bridges are absent. In all Gram-negative bacteria, the structure of the murein bag is identical (Fig. 1).

Above the single-layer murein bag lies the outer layer of the cell wall, the outer membrane. In ultrathin bacterial slices, it resembles the plasmatic membrane. The outer membrane is built of proteins, phospholipids, and lipopolysaccharides (Fig. 1), and is tight against the murein layer and bonded to it by lipoproteins. Lipoproteins are covalently bound to murein layers, apparently through diaminopimelic acid; they have an outside orientation of their lipophilic termini and are thus fixed in the lipophilic bilayer

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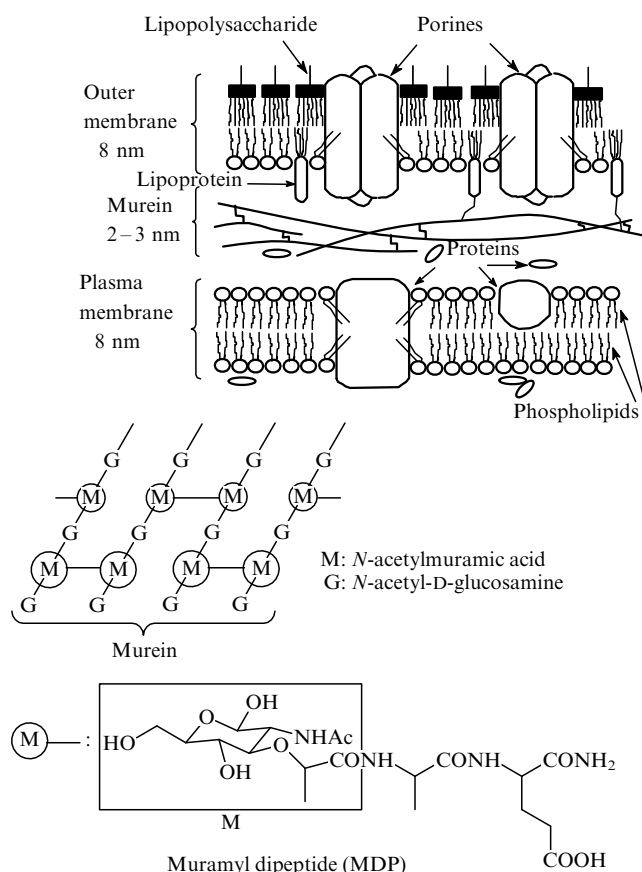


Figure 1. A structural model of the cell wall of Gram-negative bacteria. The structure of murein.¹¹

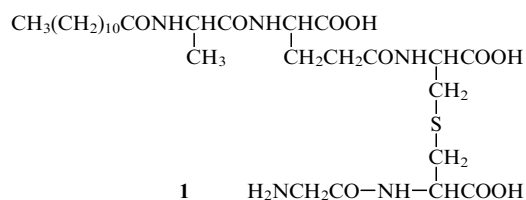
by hydrophobic interactions. This bilayer contains phospholipids and hydrophobic termini of lipopolysaccharides (lipid A); the hydrophilic termini of the latter (O-specific heteropolysaccharide side chains) are directed outside.¹⁰

By virtue of their capacity to stimulate the immune response, the components of bacterial membranes, such as murein, lipopolysaccharides, and lipopeptides have received particular attention of investigators.

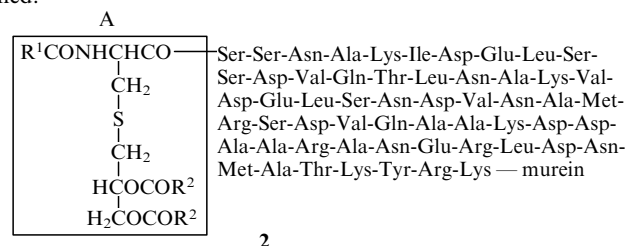
III. The lipopeptide composition of the bacterial cell wall

In contrast to peptidoglycans the main structural element of which is muramyl dipeptide responsible for the biological activity, lipopeptides are heterogenous as regards their composition and biological functions. Three groups of lipopeptides can be specified.

The first group includes lipopeptides the peptide component of which contains murein-specific amino acids, first of all, D-glutamic acid, as the main structural unit. It is this amino acid composition and sequence that determine largely the immunomodulating activity of lipopeptides-1 (LP-1). As a rule, the lipid component of LP-1 includes fatty acids that increase the 'lifetime' of the compound in the organism and favour its penetration into lipophilic compartments.¹¹ A typical representative of this group is lauroyl-L-alanyl-γ-D-glutamyl-N(6)-glycyl-lantionin (1):



Lipopeptides of the second group include fragments of a lipoprotein isolated from *E. coli*. This lipoprotein is a component of the outer membrane of Gram-negative bacteria. It contains 58 amino acid residues and is produced as a secretory precursor with a signal peptide at the N-terminus. A detailed description of this lipoprotein has been given by Braun.¹² The *E. coli* lipoprotein exhibits the mitogenic activity in higher organisms and stimulates the production of B-lymphocyte clones in murine cultures. The amino acid composition of the lipoprotein 2 has been established.¹²



R¹, R² — saturated and unsaturated alkyl.

The main structural element of the second group lipopeptides is that derived from L-cysteine and three fatty acid residues (the A-fragment of compound 2). Owing to the presence of this structural unit, the lipopeptides belonging to the second group (LP-2) can be easily incorporated into biological membranes. The amino acid composition of LP-2, in contrast to that of LP-1, can vary widely. Lipopeptides of this group are characterised by a broader spectrum of biological activity.¹¹

Group 3 includes lipopeptides possessing antibiotic activity. Many representatives of this group have a cyclic or mixed (cyclic-linear) structure of their peptide chains; the lipid component is a higher fatty acid. Many compounds of this group are produced by bacteria; the functions of the majority of lipopeptides-3 (LP-3) are associated with ion transport across membranes. LP-3 are characterised by strict specificity with respect to the producing organism, which makes them different from, e.g., the lipophilic portion of the *E. coli* lipoprotein, which may be common for most bacteria.¹¹ LP-3 do not exhibit immunomodulating properties and are not considered in more detail in this article. The information about their properties can be found in a number of reviews.^{13–15}

IV. Effects of lipopeptides on the development of early stages of the immune response

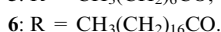
The penetration of a foreign infection into the organism causes a rapid increase in the blood level of coloni-stimulating factors (CSF). These factors are synthesised by various kinds of cells, including endothelial cells, fibroblasts, macrophages, and lymphocytes.¹⁶ Their effects on pluripotent stem cells induce, after a series of differentiation stages, the formation of large amounts of various leucocytes. They include B-lymphocytes responsible for antibody synthesis and T-lymphocytes: T-helpers (T_H) manifesting helper activity, T-suppressors (T_S) manifesting suppressor activity, and cytotoxic T-lymphocytes manifesting cytotoxic activity (T_C).¹⁶ The population of killer cells includes also natural killer cells (NK) and large granular lymphocytes (LGL).¹¹

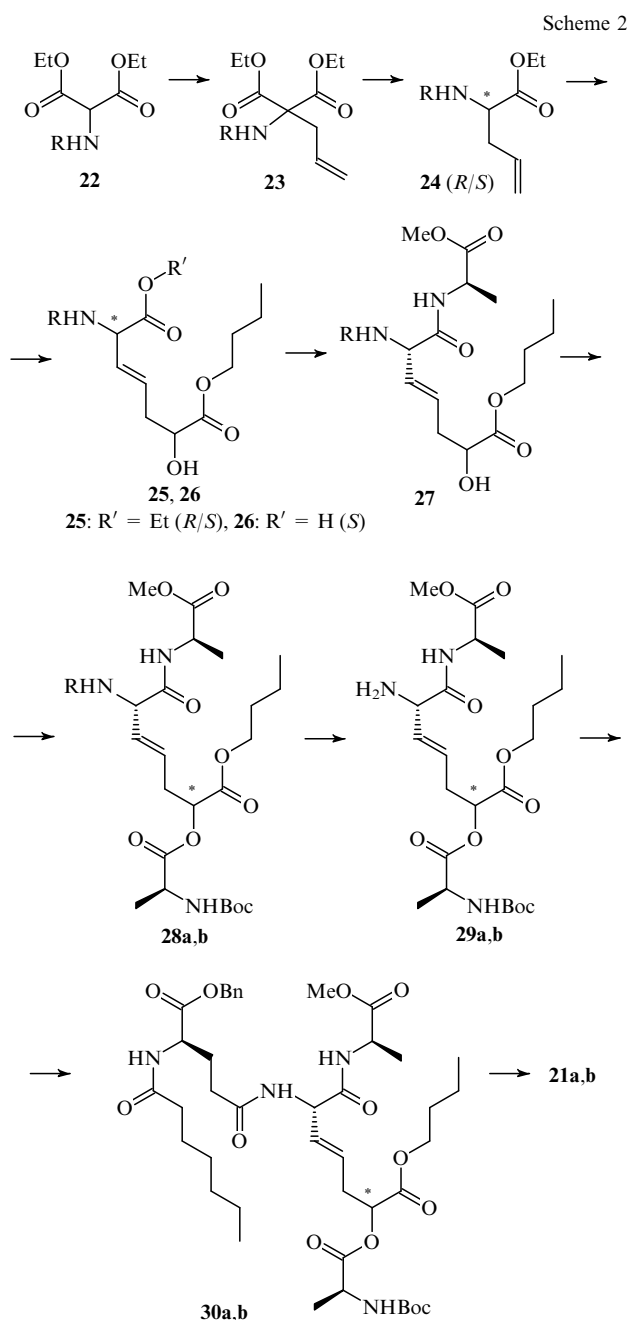
Among granulocytes, a leading role in inducing a rapid response of the organism to a foreign infection is played by neutrophils. The eosinophils (Eos) and basophils fulfil specific functions aimed at protection from parasitic organisms. Protection from bacterial and viral infections or tumour metastases is provided by monocytes (Mo) circulating in the blood and by macrophages (Mp) in tissues. The functions of these cells can be assessed using various test systems *in vivo*.

The interactions of different cells and cell systems are mediated by various factors and receptors. A prominent role in cell interactions is played by well-known factors, such as interleukins (IL-1, IL-2, IL-3, IL-4, and IL-5), colony-stimulating factors,

Immunostimulating effects produced by lipopeptides depend on the subsequent stages of the immune response. Lipopeptides stimulate phagocytic macrophages and monocytes in such a way that these cells begin to secrete factors stimulating the formation of colonies of differentiated blood cells as well as interleukin-1. The secretion of IL-1 is a signal for T-helper cells to begin proliferation. In turn, T-helper cells secrete IL-2, which stimulates the proliferation of all types of T-lymphocytes,¹⁷ as well as of IL-4 and IL-5, which in turn stimulate the proliferation and maturation of B-cells.¹¹ Interleukin-3 secreted by certain populations of T-helper cells produces a stimulating effect on the proliferation of various types of haemopoietic cells. In addition, endothelial cells (End) and fibroblasts (Fibr) begin to synthesise colony-stimulating factors. Thus the factors secreted by all these cells result in the activation of bone marrow cells that are leucocyte progenitors (Leuc. prog).¹¹ As a result, different populations of leucocytes become replenished with new cells. The increase in the number of eosinophils, cytotoxic T-lymphocytes, killer cells, and polymorphonuclear leucocytes or neutrophils (PMN) provides effective stimulation of the immune response,¹¹ since most leucocytes are destroyed while fulfilling their protective functions. Thus, the interaction of lipopeptides with monocytes and macrophages induces an immune response, which results in effective destruction

Moreover, the lauroyltripeptide **3c** was found to be as active as compound **3a**. Both compounds stimulate the production of interleukin-1 by macrophages and induce the release of CSF in the blood of mice when used in doses sufficient to protect experimental animals from bacterial infections.²³





22–27: R = COOCH₂CCl₃;
a: *R*-isomer; b: *S*-isomer.

reaction of a glyoxylic acid ester with *N*-protected 2-aminopent-4-enoic acid; this reaction is catalysed by strong Lewis acids. The 2,2,2-trichloroethoxycarbonyl group, which is stable in the presence of strong Lewis acids, was used for *N*-protection. Of the synthetic schemes proposed, that presented here (Scheme 2) was the most effective one, since it permitted the suppression of undesirable side reactions and gave the highest yields of the final products.

The protected diethyl aminomalonate **22** was treated with allyl bromide in EtOH/EtONa to give compound **23**, which was further converted into the racemic derivative **24**. The reaction of compound **24** with butyl glyoxylate gave a mixture of diastereomers **25**. Compound **25** was then hydrolysed with α -chymotrypsin to give stereospecifically the (*S*)-acid **26**, which, in turn, was coupled with the methyl ester of D-alanine to give a mixture of diastereomers **27**. The esterification of the secondary hydroxyl of compound **27** with Boc-L-alanine in the presence of dicyclohexylcarbodiimide (DCC) and dimethylaminopyridine (DMAP) gave a mixture of diastereomers **28a,b**, which could be easily separated by crystallisation or chromatography. After removal of the *N*-trichloroethoxy-carbonyl protective group at pH 4.0 and 25 °C, the corresponding amines **29a,b** were coupled with γ -carboxy group of α -benzyl *N*-heptanoyl-D-glutamate following its activation with isobutyl chloroformate. After removal of Boc-protection with trifluoroacetic acid and treatment with hydrochloric acid in ether, the lipopeptides **30a,b** were converted into the hydrochlorides of the target products **21a,b**.

Compound **21a** induced high titers of colony-stimulating factors without exhibiting toxic effects.³⁰ Unfortunately, its activity strongly declined with time, since it was rapidly metabolised after oral administration.

The hydrochloride **21c** decomposed to give mainly the inactive ester **32** (Scheme 3) and a small amount of the hydroxy compound **31**, which still exhibited immunostimulating activity.

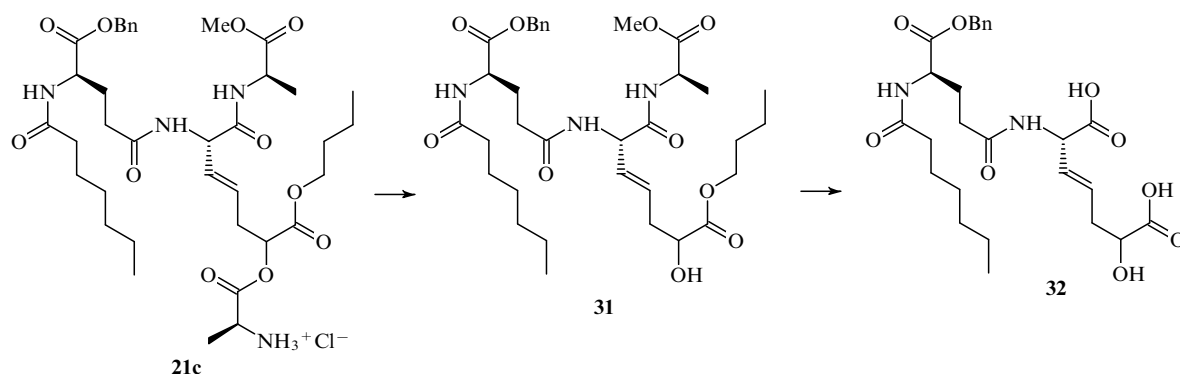
In order to prevent the rapid metabolic process inherent in compound **21**, its analogue with an additional methyl group in the α -position of the pimelic acid residue has been synthesised.³⁰

All the lipopeptides mentioned above (**3a**, **4**, **14**–**20**) are highly potent immunostimulators. The former representative of lipopeptides that contains the murein-specific amino acids, the lauroyltetrapeptide **3a**, stimulates *in vivo* the phagocytic activity of macrophages in mice and of human blood monocytes and enhances the activity of the reticulo-endothelial system in mice.^{20, 21} In mice, this compound induces cytotoxic lymphocytes against allogenic tumour cells and stimulates the activity of NK-cells in spleen and peripheral blood.

These activities indicate that the lauroyltetrapeptide can interact (directly or indirectly) with phagocytic cells, T-lymphocytes, and NK-cells. It was shown also that the lauroyl tetrapeptide stimulates *in vitro* the helper activity of human blood lymphocytes in the course of B-lymphocyte differentiation into plasmacytes.

In mice, the lauroyltetrapeptide manifests the adjuvant effect on DTH reactions and on the production of antibodies against

Scheme 3



various antigens, being more active than MDP in the former case and less active in the latter case.

The lauroyltetrapeptide **3a** induces the resistance of mice to various microbial infections (*Klebsiella pneumoniae*, *Listeria monocytogenes*) and inhibits the production of pulmonary metastases in mice inoculated intravenously with B16 melanoma cells or intradermally with Lewis lung carcinoma cells. It allows one to reduce the optimum dose of compounds exhibiting anticancer activity, e.g., cyclophosphamide. In all *in vivo* systems, the lauroyltetrapeptide **3a** exhibited activity at concentrations ranging from 0.1 to 3 mg kg⁻¹, whereas in mice intravenously immunised with this agent its LD₅₀ was 410 mg kg⁻¹.

The lipopeptide **20** and some other compounds increase the resistance of mice with normal and weakened immune systems against bacterial and fungal infections and enhance the immunotherapeutic activity in mice grafted with syngenic tumour cells.^{31,32} At present, these compounds are subject to clinical trials aimed at testing of their therapeutic utility, especially in those cases where the patient's immune system needs to be reinforced.

Owing to their immune activity, the lipopeptides can not only protect against bacterial infections but also interfere with other processes (e.g., metabolism of xenobiotics in liver) and thus prevent toxic effects of certain compounds on the organism.

The immunomodulating lauroylpeptides can protect mice against the toxic effects of paracetamol.³³ Equal doses of compounds **3a,c** manifest the immune activity, prevent the toxic effects of paracetamol (80% survival in mice), and cause a decrease in ethane exhalation, which is an index of lipid oxidation *in vivo*. Also, these lipopeptides reduced the microsomal cytochrome P-450 content in liver and suppressed CCl₄-induced lipid oxidation. The mechanism of their protective effects can be explained by the presence of factors secreted under the action of lipopeptides **3a,c**, such as interleukin-1 inhibiting the effect of cytochrome P-450³⁴ or other factors secreted by macrophages³⁵ or Kupffer cells.³⁶

VI. Lipopeptides-2

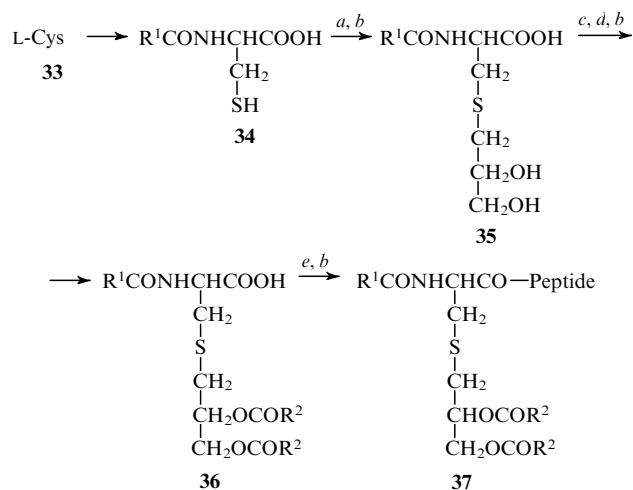
Studies on the biological activity of bacterial membrane components revealed that natural lipoproteins, particularly the *E. coli* lipoprotein and its fragments (natural lipopeptides), like the bacterial polysaccharide and muramyl dipeptide, exhibit the mitogenic activity and stimulate cells provoking the augmented release of interleukin-1, the production of prostaglandins E₂, F_{2α}, and interferon.^{37–39} In addition, the membrane lipoproteins are potent activators of polyclonal B-lymphocytes.

Synthetic lipopeptides, the analogues of natural lipopeptides, also exhibit immunostimulating activity. N-Terminal lipopeptides of the *E. coli* outer membrane lipoprotein, such as tripalmitoyl-S-glyceryl-L-Cys-Ser (Pam₃Cys-Ser) and its analogues with longer amino acid sequences⁴⁰ that stimulate the production of B-lymphocyte clones,⁴¹ were synthesised (Schemes 4 and 5).

The first step in the synthesis of *E. coli* lipoprotein analogues according to Scheme 4 was the preparation of a series of *N*-acylcysteines (**34**) from the original L-cysteine (**33**). Thus it was converted into *N*-behenoyl-L-cysteine (**34**) with 1,2-*O*-isopropylidene-3-*O*-tosyl-*sn*-glycerol and acid hydrolysis yielded *N*-behenoyl-S-[(2*R*)-2,3-dihydroxypropyl]-L-cysteine (**35**). If (*R,S*)-glycidol was used instead, a mixture of *N*-behenoyl-S-[(2*R,S*)-2,3-dihydroxypropyl]-L-cysteines was obtained. The esterification of the carboxyl group of cysteine into the benzhydryl ester and acylation of hydroxy groups were followed by deprotection using acidic hydrolysis (pH 5) yielding compound **36**.

The stage (e) requires special comment. The conventional peptide synthesis with dicyclohexylcarbodiimide and *N*-hydroxybenzotriazole resulted in a practically complete racemisation. The use of *N*-hydroxynorbornanedicarboximide instead of *N*-hydroxybenzotriazole gave compound **37**, which contained less than 3% of the (*S,R*)-diastereoisomer.¹¹

Scheme 4



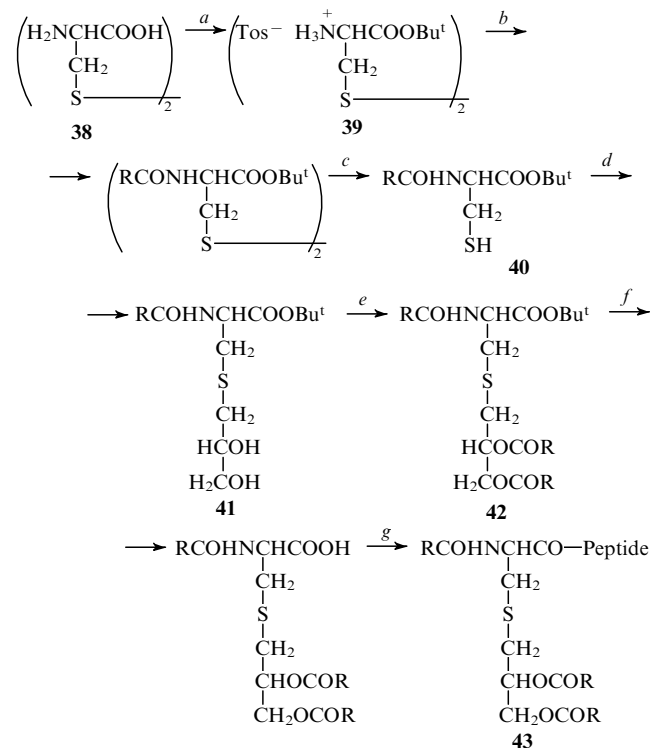
34–37: R¹ = CH₃(CH₂)₂₀;

36, 37: R² = CH₃(CH₂)₂₃.

(a) 1,2-*O*-isopropylidene-3-*O*-tosyl-*sn*-glycerol, K₂CO₃, EtOH;

(b) H₃O⁺; (c) Ph₂CN₂; (d) R²COCl, Py; (e) DCC, *N*-hydroxynorbornanedicarboximide, C-protected peptide.

Scheme 5

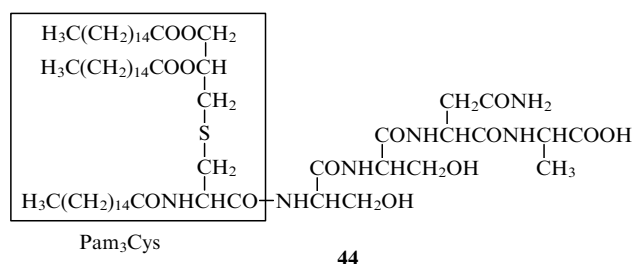


(a) MeCOOBu^t, HClO₄; (b) RCOCl, *N*-ethylmorpholine; (c) Zn, citric acid; (d) 1-*O*-tosylglycerol, DBU, DMF; (e) RCOCl, Py, 4-dimethylaminopyridine; (f) CF₃COOH; (g) DCC, *N*-hydroxynorbornanedicarboximide, peptide.

At the first step of the synthesis depicted in Scheme 5, the ester **39** was obtained from the original compound, L-cysteine (**38**). Acylation of the amino group in **39** with palmitoyl chloride and subsequent reduction of the disulfide bond with zinc in acidic medium led to the *tert*-butyl ester of *N*-palmitoylcysteine (**40**). This compound was alkylated at the thiol group with 1-*O*-tosyl-

sn-glycerol, which reacted faster than 1,2-*O*-isopropylidene-3-*O*-tosyl-*sn*-glycerol, to give compound **41**, which was acylated with palmitoyl chloride to give compound **42**. Removal of the *tert*-butyl group with trifluoroacetic acid and attachment of the peptide fragment yielded the final product **43**.

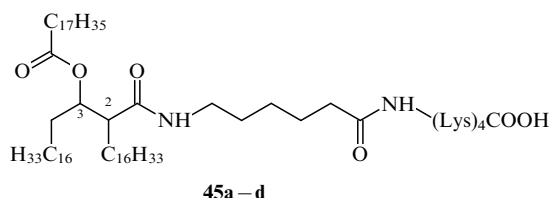
In studies^{40, 42–46} on lipopeptides with various lengths of peptide chains, number of fatty acid residues and protective groups, the objects of investigation were lipopeptide monolayers. In an effort to gain information about the interaction of these compounds with a typical lipid membrane, the monolayers of lipopeptides with three fatty acid residues were mixed with those of dipalmitoylphosphatidylcholine and cholesterol. (These studies used synthetic lipopeptides that contained only the palmitic acid residues, whereas their natural counterparts contained a mixture of higher fatty acids.⁴⁷)



It was shown that the synthetic lipopentapeptide, *N*-palmitoyl-*S*-[(2*R,S*)-2,3-dipalmitoyloxypropyl]-*L*-cysteinyl-*D*-seryl-*D*-seryl-*D*-asparaginyl-*D*-alanine (**44**) exhibited the same mitogenic properties as did the natural lipoprotein.^{45, 46, 48–50}

Even after the shortening of the peptide chain from the lipopentapeptide Pam₃Cys-Ser-Ser-Asn-Ala to the lipodipeptide Pam₃Cys-Ser, the immunostimulating properties were still retained. However, tripalmitoyl-*S*-glyceryl-*L*-cysteine as such exhibited only a weak stimulating activity.⁴¹ The lipophilic, fully protected lipopeptide Pam₃Cys-Ser(Bu^t)OBu^t manifested a weak mitogenic activity. It was therefore concluded that the crucial role in the specificity of activation is played by polar head groups, in particular by hydroxy and carboxy groups of serine. Owing to these features, the synthetic mitogens described above are highly suitable objects for the study of early events of the immune response, for the isolation of specific binding proteins, and for the analysis of structure-activity relationships.⁵¹

However, these synthetic analogues of the *E. coli* N-terminal lipopeptide have one serious disadvantage, namely, they are poorly soluble in water, which prevents their application as adjuvants. To overcome this problem, the lipopeptide tripalmitoyl-*S*-glyceryl-cysteinyl-seryl-(lysyl)₃-lysine (Pam₃Cys-Ser-Lys₄), was synthesised,⁵² which is both water-soluble and, as has been demonstrated in different tests, biologically active. Compounds **45a–d**, the derivatives of 3-*O*-stearylcorinomycinolic acid, were also synthesised.⁵³



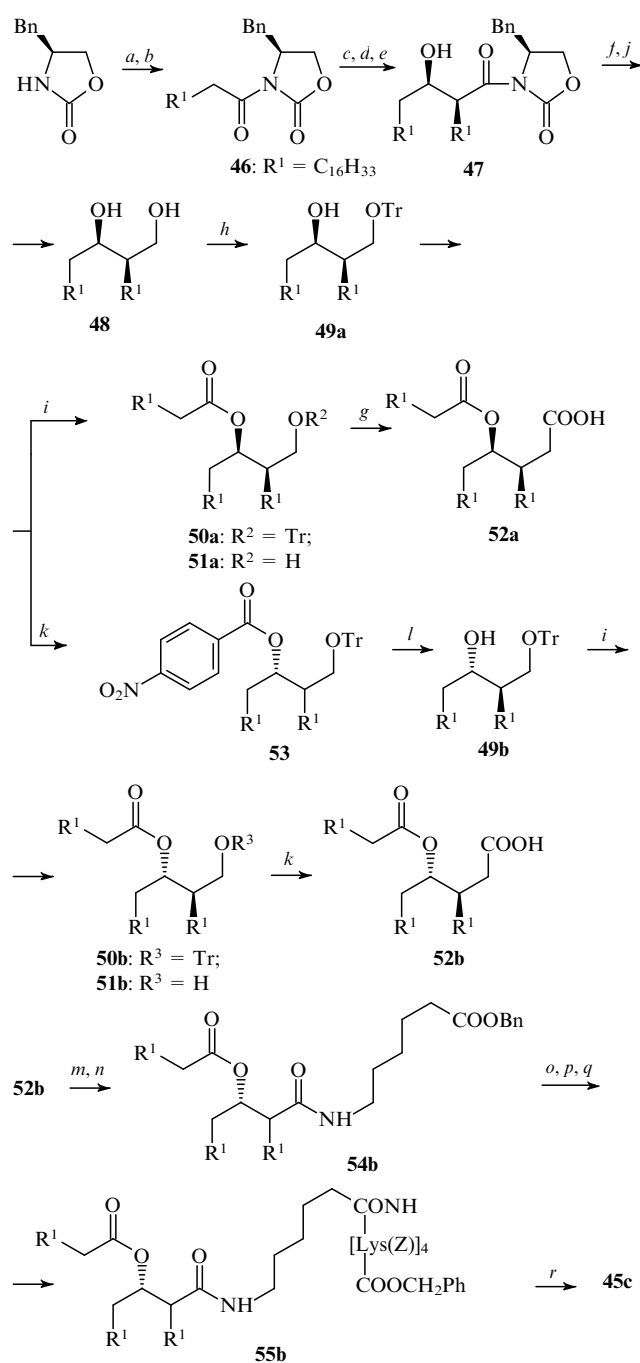
45a: (2*S*,3*R*)-isomer; **45b:** (2*S*,3*S*)-isomer;

45c: (2*R*,3*S*)-isomer; **45d:** (2*R*,3*R*)-isomer.

The main problem in the synthesis of these compounds was the elaboration of a scheme that would give all the four stereoisomers. Jacques and Grob⁵³ proposed the following paths for their synthesis (Scheme 6).

S-N-Stearyl-2-oxazolidone (**46**) was obtained by sequential treatment of *S*-4-benzyl-2-oxazolidone with butyllithium and

Scheme 6



R' = CH₃(CH₂)₁₅;

(a) BuLi, THF, –78 °C; (b) C₁₇H₃₅COCl, –78 °C; (c) 9-BBN-OTf, Pr₂NH, CH₂Cl₂, 0 °C; (d) C₁₇H₃₅CHO, –78 °C; (e) MeOH, 30% H₂O₂, buffer pH 7.0, 0 °C; (f) LiBH₄, ether; (j) NH₄Cl, 0 °C; (h) Ph₃CCl, Py; (i) C₁₇H₃₅COCl, Py/CH₂Cl₂, 0 °C; (k) KMnO₄, C₆H₁₄/AcOH/H₂O; (g) DEAD, PPh₃, *p*-NO₂C₆H₄COOH, C₆H₆; (l) 2 M NaOMe/MeOH; (m) DCC, HONSu; (n) Cl[–]NH₃⁺(CH₂)₅COOCH₂Ph, Pr₂NH, DMF/CH₂Cl₂; (o) 10% Pd/C, H₂, AcOEt; (p) DCC, HONSu, CH₂Cl₂, 0 °C; (q) Cl[–]NH₃⁺[Lys(Z)₄]COOCH₂Ph, CH₂Cl₂; (r) 10% Pd/C, H₂, THF/0.1 N HCl.

stearyl chloride. Treatment of compound **46** with 9-borabicyclo[3.3.1]nonyl trifluoromethanesulfonate (9-BBN-OTf) and condensation of the reaction product with octadecanal gave compound **47**. It was further converted into the diol **48** by

treatment with LiBH_4 in moist ether. The introduction of a trityl protection at the primary hydroxy group and acylation of the secondary hydroxy group in the diol **48** with stearoyl chloride gave compound **50a**. Removal of trityl protection to give the ester **51a** was complicated by intramolecular acyl migration. However, subsequent oxidation of the isomer mixture gave the acid **52a**.

The acid **52b** was obtained by inversion of the stereochemistry in compound **49a** at C(3). This compound was converted into the ester **53** by interaction with *p*-nitro-(or *o*-nitro-)benzoic acid in the presence of PPh_3 and diethyl azodicarboxylate (DEAD). Its de-esterification required drastic conditions [stage (I) in Scheme 6] and resulted in compound **49b**, which was then converted into the acid **52b** by analogy with compound **49a** $\rightarrow$ **52a**. The same reaction sequence, which began with (*R*)-4-benzyl-2-oxazolidone, gave the enantiomers of compounds **46**, **47**, **48**, and **53**, respectively, and the final products **52c** (2*R*,3*S*) and **52d** (2*R*,3*R*). Further, the peptide fragment was attached to acids **52a–d** with the use of the active esters method to give the lipopeptides **45a–d** [stages (*m–r*) in the Scheme 6].

However, these lipopeptides have four lysine residues, which cause certain difficulties due to the formation of high positive charges.

In the study by Kleine *et al.*,⁵⁴ two lipopeptide analogues of the *E. coli* lipoprotein, Pam_3CysOH and $\text{Pam}_3\text{Cys-SerOH}$, were conjugated with polyoxyethylene 3000 (POE) to increase the solubility of lipoproteins. The conjugates obtained possessed high solubility in water and were devoid of the formation of high positive charges. The increase in the solubility did not bring about any significant changes in the biological properties of the lipopeptide fragment. It was concluded that the polyoxyethylene component, which is inactive itself, enhances the activity of lipopeptides by increasing the percentage of lipopeptide molecules accessible to the cells.⁵⁴

VII. Possible applications of lipopeptides-2

The lipopeptide fragments of the *E. coli* membrane lipoprotein are highly effective stimulators of antibody production and activators of B-cells. Synthetic lipopeptides enhance primary and secondary immune responses to corpuscular antigens *in vitro* and *in vivo*.⁵⁵ The addition of synthetic lipopeptide fragments to acetone-killed cells of *Salmonella typhimurium* makes it possible to significantly reduce the vaccine dose. It is believed that the first step in the mechanism of action of lipopeptides is their interaction with the cell plasma membrane through incorporation of lipophilic groups into the lipid bilayer and their binding to membrane proteins. Hence, the mitogenic activation of cells can be achieved through the use of conditions of a serumless culture and the use of a mitogen that is optimally dissolved in detergent-containing solutions. Under these conditions, the mitogenic activity of compound **44** *in vitro* can be observed at as low concentrations as *e.g.* 10 ng ml^{-1} . The optimum stimulating activity was observed at concentrations around 30 mg ml^{-1} .

The adjuvant properties of the tripalmitoylpentapeptide with respect to the immune response was studied *in vitro*.⁵⁶ The immune response to sheep erythrocytes (both native and nitrophenol-treated) was strongly enhanced after the addition of various amounts of the tripalmitoylpentapeptide **44** to cell cultures. This effect was dose-dependent, the optimum adjuvant effect being manifested at the concentration range of $10–30 \text{ mg ml}^{-1}$.

A sharply pronounced adjuvant effect was observed in only those cases when the tripalmitoylpentapeptide and the antigen acted simultaneously; the addition of the lipopeptide either 24 h prior to, or 24 h after, the addition of the antigen had no effect. Hence, the adjuvant effect of the tripalmitoylpentapeptide can be associated with the formation of an adjuvant-antigen complex.

The use of lipopeptides as adjuvants is not confined to cell antigens *in vitro*. It was shown that the *in vivo* immune response to native and nitrophenol-treated sheep erythrocytes was also enhanced significantly in the presence of the lipopeptide; the *in*

vivo immune response to proteins, like ovalbumin, can also be increased after the addition of the lipopeptide.

Of special interest were the studies on the mitogenic and adjuvant activities of water-soluble lipopeptides, since in the case of high immunostimulating activity these compounds might be used commercially. $\text{Pam}_3\text{Cys-Ser-POE}$ and $\text{Pam}_3\text{Cys-POE}$ were assayed for mitogenic activity towards human B-lymphocytes *in vitro* and for adjuvant activity in mice *in vivo*. It was established that polyoxyethylene-lipopeptide conjugates exhibit the same mitogenic activity as does the water-soluble cationic lipopeptide $\text{Pam}_3\text{Cys-Ser-Lys}_4$. They exhibited biological activity even at concentrations around 30 mg ml^{-1} .

In order to investigate possible areas of the application of lipopeptide-polyoxyethylene conjugates as adjuvants for the construction of vaccines, the adjuvant activities of these compounds were compared to those of three commercially available adjuvants: Freund's adjuvant, Hunter's Titermax, a nonionic block copolymer,⁵⁷ and vegetan extracted from potatoes. Ovalbumin and synthetic melittin (a 26-membered bee venom polypeptide) were used as the antigens. The polyoxyethylene-lipopeptide conjugates were less active than $\text{Pam}_3\text{Cys-Ser-Lys}_4$ or Freund's adjuvant, while their activities were comparable with that of the Hunter's block copolymer or vegetan. In mice immunised with the antigen (ovalbumin or melittin) and $\text{Pam}_3\text{Cys-Ser-POE}$ or $\text{Pam}_3\text{Cys-POE}$, the antibody titers against both melittin and ovalbumin were similar. However, the maximum immune response (compared to that raised with the Freund's adjuvant) required repeated immunisations. In most cases, three injections were sufficient for this purpose.

The design of synthetic vaccines requires that the demand of safety of polyclonal activators used as adjuvants for routine immunisations be met. The lipopeptides tested did not exhibit any toxic or other undesirable effects in animal studies, they evoked only a 7-days-lasting inflammation at injection sites with a complete recovery of the injured area after several weeks. By contrast, animals immunised with the Freund's adjuvant developed long-lasting granulomas at injection sites.

It was thus concluded⁵⁴ that the new polyoxyethylene compounds are capable of polyclonal activation of human B-lymphocytes in culture systems and exhibit a sufficiently high adjuvant activity. They can be easily synthesised and yield stable solutions. In addition, they are non-toxic. It was therefore decided to continue the use of $\text{Pam}_3\text{Cys-Ser-POE}$ and $\text{Pam}_3\text{Cys-POE}$ as adjuvants for immunisation of animals and, after conducting appropriate tests, of human beings as well.

The synthetic mitogen tripalmitoylpentapeptide **44** and some of its analogues can non-specifically enhance the resistance of a host organism to bacterial infections. This property is particularly often exploited in studies aimed at a search for new effective antigens in the design of synthetic vaccines when a low-immunogenic peptide or a fragment of a natural protein are to be used as antigens. Since the procedure of covalent binding of a peptide and the lipopeptide adjuvant increases immunogenicity and can be easily performed, it can be used in studies of epitope specificity of various natural proteins. An example is the study by Beck-Sickinger *et al.*,⁵⁸ which is dedicated to the discovery of effective antigens against *Haemophilus influenzae* (Hi).

The *Haemophilus influenzae* type b (Hib) is the main causative of endemic bacterial meningitis in newborns and children; the non-typeable Hi is also a potent pathogen. The most severe bacterial infections in humans (meningites, arthrites, *etc.*) are caused by Hib. The antibodies against the Hib capsular polysaccharide protect humans from diseases caused by Hi. However, this way of protection is ineffective in children under one year of age who are at the highest risk of being infected with these diseases. These facts have stimulated interest in the search for other antigens.

The P6 protein (16 600 Da), which is present in the outer membrane of two typeable and one non-typeable Hi strains, is the most important antigen in raising the immunity against Hi.

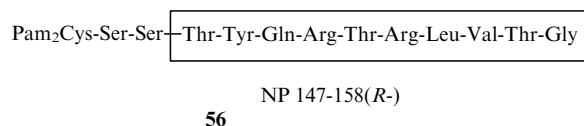
Antibodies against P6 possess protective and bactericidal activities. The progenitor of P6 is a bacterial lipoprotein containing 134 amino acid residues and having at its N-terminus fatty acids linked by an amide and ester bonds to *S*-glycerylcysteine. Since this structure resembles the *E. coli* lipoprotein, lipopeptides were synthesised⁵⁸ in which different fragments of the amino acid sequence of P6 were covalently linked to *N*-palmitoyl-*S*-[(2*R,S*)-2,3-dipalmitoyloxypropyl]-L-cysteinyl-D-serine. This study has made it possible to establish the epitope specificity of antibodies. Lipopeptides containing the sequence Gln-Ile-Leu-Asp-Ala-His-Ala-Ala (P6 47-54) and the murine B-cell epitopes Gly-Glu-Tyr-Val (P6 43-46) were able to induce T-helper activity in BALB/c mice. The antibodies raised in the immunisation could adequately neutralise the Hi bacteria. Thus the use of a mixture of lipopeptides containing the above segments of the P6 protein as synthetic vaccines holds much promise for *in vivo* studies of model infection systems.

Another example of the use of adjuvants covalently bound to antigens can be found in the study carried out by Deres *et al.*⁵⁹ The covalent binding of lipopeptide adjuvants to antigens is especially advantageous for compounds that exhibit low immunogenic activity by themselves. Lipopeptides used as adjuvants enhance the immunogenic activity of antigens in synthetic vaccines.

Cytotoxic T-lymphocytes make an appreciable contribution to immunity against intracellular pathogens. This refers also to viral infections, where cytotoxic T-lymphocytes recognise viral peptides presented by molecules of the major histocompatibility complex (MHC) class I on the surface of infected cells.⁶⁰ The induction of virus-specific cytotoxic T-lymphocytes usually requires *in vivo* priming with infectious viruses. Inactivated viruses, like viral proteins or peptides, are mostly ineffective as inducers of the cell-type immune response *in vivo*, although these antigens can initiate antibody production against viral antigens.

The absence of the anticipated effect following the use of peptides as antigens can be assigned to the 'non-physiological' type of the antigen presentation (the lack of conjugation with MHC glycoproteins), since T_C can usually recognise the fragments that are derived from proteins endogenously produced by target cells but are incapable of recognising the free peptides that are not bound to the glycoproteins of the major histocompatibility complex.⁶¹ The second reason is the lack of secondary signals, such as cytokins, released by antigen-presenting cells.

Unlike native peptides, synthetic compounds attached to a lipophilic anchor (lipopeptides) can activate virus-specific cytotoxic T-lymphocytes *in vivo*.⁵⁹ The structure of one such lipopeptide, the epitope of the influenza virus nucleoprotein, which is the most adequately recognised by H-2d-restrictase [peptide NP 147-158(*R*-)], conjugated with Pam₃Cys-Ser-Ser, is given below (see formula 56).



The precise mechanism of the *in vivo* activation of cytotoxic T-lymphocytes by lipopeptides is still unknown. A possible reason for this effect is that the anchor molecule of Pam₃Cys possesses the ability to activate accessory cells that secrete factors needed for the differentiation of cytotoxic T-lymphocytes.⁵⁹ If this is true, a mixture of Pam₃Cys and a native peptide can also be used for the activation of cytotoxic T-lymphocytes.

If the effect of lipopeptides is not determined by the non-specific action of accessory cells and/or T-helper cells, other possibilities may be offered. Probably, the lipid anchor prolongs the lifetime of the antigen molecule *in vivo* relative to native peptide molecules. At the same time, it is not excluded that the lipid anchor attaches to the cell membrane and thus favours the binding of the antigen with glycoproteins of the major histocom-

patibility complex class I, thus offering a more 'physiological' path of antigen presentation.

The major problem, which restricts the use of peptide vaccines in natural populations, is that T-cells in individuals with different MHC always recognise different peptides from viral proteins together with their own corresponding MHC. Thus, universal synthetic vaccines stimulating the growth of populations providing the cell-type immune response to a certain viral antigen should contain all of the relevant epitopes recognised by T-cells. The fulfilment of this condition is not a very difficult task because of the relatively good availability of synthetic Pam₃Cys-Ser-Ser-peptide conjugates. Pam₃Cys-Ser-Ser covalently linked to peptides is particularly suitable for the design of vaccines, since the production of neutralising antibodies, another important element of the antiviral immunity, can also be achieved through the conjugation of Pam₃Cys-Ser-Ser to the corresponding epitopes.

VIII. The use of lipopeptides-2 in the fight against the human immunodeficiency virus

The problem of infection of humans with the immunodeficiency virus presently becomes a formidable challenge; therefore, many recent studies deal with the development of vaccines against the immunodeficiency virus, which can induce antibody synthesis and simultaneously elicit associated cytotoxic responses.

Vaccinations against the human immunodeficiency virus (HIV) with the use of inactivated viruses raises the problem of their therapeutic safety for human beings. The use of viral genes in the composition of recombinant vectors also requires further investigation. Peptide vaccination is a very promising approach; however, free peptides are often little immunogenic. The interest in lipopeptide vaccines is not incidental for these reasons. Their use is devoid of side effects, and this vaccination can be applied to humans. Moreover, the immune response induced will be free from that against the vector molecule, as is the case with recombinant vaccines. Therefore, the combination of lipopeptides inducing the cell-type response with lipopeptides stimulating antibody production will provide effective protection against the immunodeficiency virus.

The study carried out by Loleit *et al.*⁶² is an example of the use of lipopeptides for immunisation against HIV. These authors found that the C-terminal segment of the reverse transcriptase (RT) of HIV 1 contains a highly immunogenic determinant that causes the proliferation of T-cells in different mouse strains and partly overlaps with the B-cell epitope. The lipopeptide *N*-palmitoyl-*S*-[(2*R,S*)-2,3-dipalmitoyloxypropyl]-L-cysteinyl-D-seryl-D-serine was used as the adjuvant, for it does not exhibit toxic effects characteristic of Freund's adjuvant and increases the immunogenicity of free peptides.⁵²

In order to assess the ability of the lipotripeptide Pam₃Cys-Ser-Ser to enhance peptide-specific immune responses *in vivo*, Loleit *et al.*⁶² have immunised mice of different strains (BALB/c, C3H/HeJ, C57BL/6) with the 22-meric conjugates Pam₃Cys-Ser-Ser-[RT-(522-543)] and Pam₃Cys-Ser-Ser-[RT-(528-549)] of the reverse transcriptase of HIV-1, which contain the T-helper epitope [RT-(528-543)] of the reverse transcriptase. The results of this study⁶² indicate that Pam₃Cys-Ser-Ser is an effective adjuvant capable of inducing T-helper and B-cellular responses to peptide sequences that represent the fragments of the C-terminal region of the reverse transcriptase of HIV-1.

The procedures used for the attachment of lipids or lipopeptides to HIV-derived peptides were also described by other groups of investigators.^{63,64} Thus, Martinon *et al.*⁶³ used the C₁₄-fatty acid peptide (HDA) as well as C-terminal fragments of peptides from the V3 region of a nucleoprotein epitope corresponding to the outer envelope proteins of HIV-1 (Env). Defoort *et al.*⁶⁴ synthesised the lipopeptide Pam₃Cys and modified it through a lysine spacer with four molecules of the HIV-1 Env-peptide to obtain the so-called multiplet antigenic system (MAPS). Both

products could induce antibody production and a cytotoxic response to HIV.

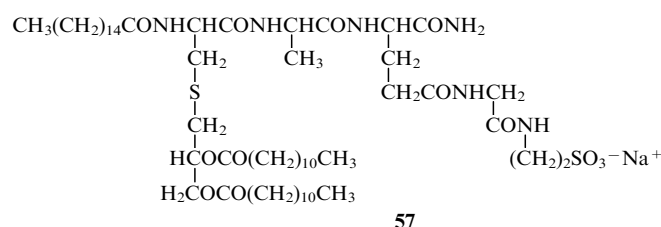
According to the most recent data, some peptides can be recognised in both mice and humans.⁶⁵ In order to assay the epitope of the reverse transcriptase RT-(528-549) for immunogenicity towards human T-lymphocytes, Loleit *et al.*⁶² have studied T-cell responses in HIV-infected individuals. The first analyses of cytotoxic responses to the C-terminal region of reverse transcriptase of HIV-1 revealed that the lipopeptide Pam₃Cys-Ser-Ser-[RT-(528-549)] could be recognised by cytotoxic T-lymphocytes of patients at different stages of the disease.

Thus, the ability of lipopeptide conjugates to induce efficient humoral and T-cell responses and the lack of toxic effects makes them probable candidates for the components of synthetic vaccines designed for use in humans.

IX. The antitumour activity of lipopeptides-2

Another important aspect of the biological action of *E. coli* cell wall lipopeptides is their antitumour activity.^{66, 67}

The modification of their peptide residues with taurine yielded compounds that were highly active *in vivo* and could destroy pulmonary metastases. One of these compounds is the sodium salt of *N*-hexadecanoyl-*S*-[(2*R*)-2,3-didodecanoyloxypropyl]-*L*-cysteiny-*L*-alanyl-*D*-isoglutamyl-glycyl-*L*-taurine **57** (CGP 31362).



Its synthesis is similar to that of compound **44** and its analogues (Schemes 4 and 5). The peptide fragment of compound **57** was modified with taurine, which imparted to it a greater polarity.^{68, 69}

Compound **57** can be incorporated into membranes of phospholipid liposomes.⁶⁹ Liposomes are unique carriers for targeted delivery of biologically active substances to phagocytosis-active cells *in vivo*. This delivery results in the activation of phagocytes and, correspondingly, in the destruction of established lung, lymphoid, and liver metastases. Like other circulating particles, liposomes are rapidly ingested by free and fixed phagocytic cells. The advantage of such physiological 'death' of liposomes is that they deliver immunomodulators to cells of the reticulo-endothelial system.

Compound **57** incorporated into liposomes can activate human blood monocytes as well as mouse peritoneal and bone marrow macrophages.⁷⁰ Periodical injections of this compound caused *in situ* activation of macrophages.⁷¹ Noteworthy, macrophages that phagocytised liposomes with incorporated compound **57**, retained their antitumour activity over a period of several days, thus favouring the destruction of established cancer metastases.

Compound **57** is a more potent anticancer agent in comparison with muramyl-peptide derivatives, since it stimulates the antitumour activity at lower doses and activates monocytes in the absence of γ -interferon. Monocytes stimulated by compound **57** exhibit both the activity related to tumour necrosis and interleukin-1 activity, whereas monocytes stimulated by muramyl-peptides manifest only tumour necrosis activity.

On the basis of numerous experiments, Utsugi *et al.*⁷¹ concluded that compound **57** can efficiently stimulate macrophages responsible for the lysis of tumour cells; this compound is a better activator of monocytes and macrophages than muramyl-peptides.

X. Conclusion

The data considered in this review show the increasing interest in the components of bacterial membranes, specifically, in lipopeptides.

The synthesis of analogues of bacterial lipopeptides is related to the fine organic synthesis of complex conjugates. This can be exemplified by the above-described methods of synthesis of compound **44** and its analogues containing a peptide fragment and three fatty acid residues. The synthesis of compounds of a mixed composition makes a contribution to the development of organic synthetic chemistry.

Since lipopeptides are optically active compounds, their synthesis brings about a number of specific problems associated with their preparation. So far the synthesis of the majority of lipopeptides is marked by complexity and multiphasity. Unfortunately, these difficulties are an obstacle on the way to the elaboration of a large set of modified analogues of natural compounds for research purposes.

A study of the biological activity of lipopeptides that are the components of bacterial membranes permits to expand the view of both the structural organisation of membranes and the activity of compounds of a mixed composition in the fight against various infections.

The pharmacological effects of natural lipopeptides and their synthetic analogues have been demonstrated in animal models *in vivo*. In addition to immunomodulating properties, lipopeptides exhibit antitumour activity and have been extensively used in recent years in the fight against the human immunodeficiency virus.

As lipopeptides do not possess toxic properties, it may be assumed that compounds of this class will find wide use in the design of contemporary synthetic vaccines as well as in the treatment of malignant tumours and autoimmune diseases.

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On the way to carbon nitride

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Abstract. The available data on the problem of hypothetical crystalline carbon nitride are considered. These involve the crystal structure, the nature of chemical bonding, and physical properties of carbon nitride of which the most interesting is its predicted high hardness comparable with that of diamond. The experiments aimed at synthesising carbon nitride are described, and properties of the materials obtained are characterised. The results of thermodynamic calculations pertinent to carbon nitride and processes of its synthesis are discussed. The bibliography includes 144 references.

I. Introduction

An extensive class of materials have been synthesised on the basis of metal and non-metal nitrides, and these materials have wide application in various areas of science and technology.^{1,2} The existence of carbon nitride is highly probable, since carbon and nitrogen can form strong chemical bonds with each other, in particular, single bonds. Various chemical compounds (including polymers) composed solely of carbon and nitrogen are known.^{3,4} Elements, such as boron, aluminium, silicon, and phosphorus readily form nitrides, which are used to produce valuable ceramics. However, for carbon surrounded by the above-mentioned elements in the Periodic Table no corresponding nitride has been obtained so far. It is surprising that until very recently the problem of carbon nitride synthesis had not even been raised. An exception is the work of Franklin⁵ who heated mercury thiocyanate to obtain a voluminous solid residue close in composition to C₃N₄, though containing from 0.6% to 2.4% hydrogen. The author called this product carbon nitride but did not study its structure and properties.

II. Theoretical analysis. Chemical bonding, crystal structure, and predicted properties

The fundamental studies of Cohen and Liu^{6–8} were initially aimed at the development of methods allowing prediction of some properties of solids on the basis of readily accessible data. One of such important properties is the bulk modulus (B) determined by the relation

$$B = -V \frac{dp}{dV} = V \frac{d^2u}{dV^2}, \quad (1)$$

where V , p , and u are volume, pressure, and energy, respectively. Theoretical analysis of the effect of covalence on the bulk modulus of semiconductors and insulators of the type of diamond and zinc blende with the tetrahedral structure showed that for the compounds composed of elements situated in the middle of the Periodic Table the magnitude of B depends only on the distance d between the nearest-neighbour atoms and is determined by a very simple relation⁶

$$B = 1761d^{-3.5}, \quad (2)$$

where B is expressed in GPa and d , in Å. For compounds composed of Group III and IV elements, this formula provides fairly acceptable values: as a rule, deviations from the experimental data are close to 2% (*e.g.*, 2.6% for gallium arsenide). At the same time, for materials including Group II and VI elements the deviation is markedly larger: for example, it reaches 14.4% for zinc sulfide. The deviations are due to the fact that formula (2) has been proposed⁶ only for compounds with non-polar bonds. If the chemical bonds in a crystal are polar, the bulk modulus is determined not only by the distance between the nearest neighbours but also by the above-mentioned polarity, which is taken into account by introducing an empirical term into the formula (2)

$$B = (1971 - 220\lambda)d^{-3.5}. \quad (3)$$

Here, B is expressed in Mbar, and the parameter λ accounts solely the extent of bond ionicity: $\lambda = 0$ for the elements of Group IV (*e.g.*, for carbon in the diamond form); $\lambda = 1$ for materials composed of Group III and V elements (boron nitride, gallium arsenide, indium phosphide, *etc.*); finally, $\lambda = 2$ for compounds

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including Group II and VI elements (cadmium and zinc sulfides, selenides, tellurides). Comparison of experimental data for 25 materials (chemical elements and binary compounds of the AB type) has shown⁷ that formula (3) allows the prediction of the magnitude of bulk moduli with a fairly acceptable accuracy.

The importance of the formula (3) is determined not only in that it allows the calculation of bulk moduli, but also in that it indicates the direction of search for new superhard materials: obviously, one should seek for minimum interatomic distances and nonpolar chemical bonds. Already in 1985 it was mentioned that the above requirements may be met by a hypothetical carbon–nitrogen compound with the tetrahedral structure;⁶ however, only in reports,^{8,9} which stimulated all subsequent studies, the problem of crystalline carbon nitride synthesis was clearly formulated with the prediction of its unusual chemical properties.

The crystal of β -silicon nitride has served as the prototype. In this compound, formal substitution of carbon atoms for silicon leads to a hypothetical structure called by analogy β -carbon nitride. In this crystal, the unit cell is hexagonal and contains 14 atoms (*i.e.*, it is a dimer of carbon nitride C_3N_4 with the stoichiometric formula C_6N_8). The carbon atoms are in the centres of slightly distorted tetrahedra, whereas the nitrogen atoms have a nearly planar-trigonal configuration. This results in a complex array of CN_4 tetrahedra linked through their apexes. In this lattice, the carbon and nitrogen atoms are in sp^3 - and sp^2 -hybridisation, respectively. Alternatively, this structure, belonging to the hexagonal space group C_{6h}^2 may be regarded as a combination of distorted layers. It may also be considered as a network of 6-, 8-, and 12-membered rings of alternating carbon and nitrogen atoms¹⁰ and as the structure of the phenacite (Be_2SiO_4) type of 3-, 4-, and 6-membered rings formed by the CN_4 tetrahedra.¹¹

Non-empirical quantum-mechanical calculations of β - C_3N_4 carried out by the pseudopotential method within the framework of localised orbitals formalism^{8,9} have shown that the length of the C–N bond is 1.47 Å. This magnitude correlates well with the sum of the tetrahedral covalent radii of carbon and nitrogen. The energy of cohesion was found to be 81 eV per unit cell or 5.8 eV per atom (see Ref. 8) (the value of 81.5 eV for the energy of cohesion per unit cell was given in Ref. 9). Representation of the total energy as a function of volume in the Murnaghan and Birch equation of state has permitted computation of the bulk modulus, which proved to be 4.27 ± 0.15 Mbar. The determination of the bulk modulus requires that formula (3) be refined taking into account that the carbon and nitrogen have different coordination numbers equal to 4 and 3, respectively. The resulting formula¹² is

$$B = \frac{N_c}{4} \frac{1972 - 220\lambda}{d^{3.5}}, \quad (4)$$

where, in contrast to the formula (3), B is expressed in GPa rather than in Mbar and N_c is the mean coordination number. In the case of C_3N_4 , $N_c = 3.43$, $d = 1.47$, $\lambda < 1$ and, depending on the λ value and according to work,¹² $B = 410$ – 440 GPa, which correlates well with the above value.

Thus, the predicted bulk modulus of β -carbon nitride is comparable with that of diamond (443 GPa). It will be shown below that somewhat different calculations give different values of the bulk modulus, and in some cases it proves to be higher than that of diamond. However, even if it is not so, most of the calculations indicate that β - C_3N_4 shifts boron nitride, the second hardest compound after diamond ($B = 369$ GPa⁷), to the third position. To get a more complete picture, note that for solidified noble gases $B = 1$ – 2 GPa, for ionic solids $B = 10$ – 60 GPa, for non-transition metals $B = 2$ – 100 GPa, for transition metals $B = 100$ – 300 GPa, and finally for covalent solids $B = 100$ – 443 GPa.¹² It is the high predicted hardness of carbon nitride (close to a record value) that stimulated further studies. According to the formulas (3) and (4), such a high hardness is due to small interatomic distances and low polarity of the C–N bond.¹³ The predicted very high energy of cohesion of β -carbon

nitride gives hope that its existence may well be realised, at least as a metastable phase.

The above-mentioned quantum mechanics calculations of the β - C_3N_4 crystal (see Refs 8 and 9) yielded maps of the electron density distribution. In particular, it turned out that the valence electrons are localised between the carbon and nitrogen atoms in such a way as to form two electron density maxima: the larger maximum near the nitrogen atom and the smaller one near the carbon atom. The values of electron density normalised to the number of valence electrons in a unit cell are 4.6 and 2.7, respectively. It also followed from the calculations that, as regards its polarity, the C–N bond in β - C_3N_4 is intermediate between the bond in the purely covalent diamond and that in the partially ionic boron nitride. It is of note, that the local electron density maximum near the carbon atom is nearly the same as in diamond. Consequently, no substantial charge transfer along the C–N bond takes place in carbon nitride, and this in turn means that the charge density asymmetry along the C–N bond is due to the non-bonding electrons of nitrogen.

Yet another interesting property is the high mean volumetric sound velocity in β - C_3N_4 making up 1.1×10^6 cm s^{−1}.⁹ This is 20% higher than in β - Si_3N_4 and is also indicative of high thermal conductivity of β - C_3N_4 determined by its high Debye temperature.¹²

It has been noted (see, *e.g.* Ref. 14) that the nitrogen atoms in β - C_3N_4 are not equivalent. There are two sorts of these atoms — N_1 and N_2 . Atoms N_1 (they account for a quarter of all nitrogen atoms) are in the centres of equilateral triangles with their apexes occupied by the carbon atoms. The nitrogen atoms are surrounded by three carbon atoms whose location is little different from the planar one. The distances between N_1 – N_1 and N_2 – N_2 are 2.46 and 2.69 Å, respectively. These distances are not large; therefore, repulsive interactions are possible for the pairs of unshared electrons of the nearest nitrogen atoms. The above interactions were determined by non-empirical quantum-mechanical calculation and found to be 1.13 and 0.67 eV for N_1 – N_1 and N_2 – N_2 , respectively.¹⁴ As a result, the crystal is destabilised by 2.14 eV per monomer chain of C_3N_4 . The above statement does not rule out the possibility of β - C_3N_4 existence as a metastable phase, though it is indicative of its definite energy loading.

The structure of β - C_3N_4 was the first that has been proposed for the crystalline carbon nitride. It is not, however, the only possible one. Although it has been noted⁸ that a simple structure of the zinc blende type is energetically unfavourable, because the first antibonding zone is occupied, subsequent quantum-mechanical and molecular-dynamic calculations pointed to the possible existence of rather diverse crystalline modifications of carbon nitride.

α -Carbon nitride, which is topologically equivalent to α -silicon nitride, was studied by the method of density functional in the approximation of the local density for the exchange and correlation of electrons.¹¹ Its structure may be described as an ABAB... sequence of packed layers of β - C_3N_4 (A) and their mirror reflections (B). The unit cell contains 28 atoms, *i.e.* it corresponds to the formula $C_{12}N_{16}$ (tetramer of C_3N_4). The dependences of total energy on volume for α - and β - C_3N_4 are very similar. Nonetheless, the α -form was found to be somewhat more favourable energetically, by 0.266 eV per monomer unit.

Analysis of α - and β - C_3N_4 has been carried out¹⁵ by the non-empirical Hartree–Fock method in the 6-31G** basis set. In this case, special attention was given to the optimisation of geometry of the molecule and to the realisation of a pyramidal configuration of the nitrogen atom as, for example, in trimethylamine rather than of a planar one as has been assumed.^{8,9} On the one hand, optimisation of the β - C_3N_4 geometry did not lead to substantial changes in its configuration: it still remained close to the planar one. Accordingly, the crystal energy was not strongly changed: it decreased in the optimisation by 4.4 kcal per monomer unit. On the other hand, considering the possibility of pyramidal configuration of the nitrogen atom in α - C_3N_4 , the optimisation was

found to result in the lowering of the crystal energy by 54.0 kcal per monomer unit. It was inferred from the calculations that α -C₃N₄ is more stable than β -C₃N₄.^{11, 15} However, the difference of energies reported in Ref. 15 proved to be larger than that in Ref. 11: it was 25.1 kcal per monomer unit for the optimised structures. The values of bulk moduli calculated recently¹⁵ are noticeably lower than those found in the previous studies. For example, for the optimised and non-optimised structures of β -C₃N₄ they were 250 and 357 GPa, respectively. Certainly, these values are also rather high but still they are much smaller than for diamond. Yet another important result of the studies cited¹⁵ is that the bulk modulus proved to be very sensitive to the geometric configuration of the nitrogen atom.

Optimisation of the geometry of α -C₃N₄ yielded yet another interesting result. The calculations have shown that the tetrahedral lattice of α -C₃N₄ contains spheroid cavities 4.1–5.2 Å in diameter with pyramidal nitrogen atoms inside. This crystal should be characterised by a negative Poisson ratio: stretching of crystal in any direction should lead to its expansion in the perpendicular direction. The phenomenon of the negative Poisson ratio is known. It was observed, for example, for α -cristobalite, when it was stretched in definite directions.^{16, 17}

The conclusions made in the work cited¹⁵ are interesting but not indisputable because of insufficient accuracy of the current computational techniques. The results of molecular-dynamic simulation¹⁸ (in accordance with the data of Refs 8 and 9) confirmed the planar configuration of the nitrogen atom in β -C₃N₄. In the case of α -C₃N₄, one half of nitrogen atoms proved to be in the planar configuration, whereas the second half was found to be in the pyramidal configuration with a bond angle C–N–C of 115°, high values of the bulk moduli being obtained for both α - and β -C₃N₄. Thus, the problem of the structure of α -C₃N₄ remains to a considerable extent open.

Cubic carbon nitride¹¹ is similar to willemite-II (high-pressure phase of Zn₂SiO₄). It can be obtained when zinc and silicon in willemite-II are replaced by carbon, and oxygen is replaced by nitrogen. Relevant calculations show that the pressure of the α -C₃N₄ transition to the cubic form is 68 GPa. Of all C₃N₄ modifications, cubic carbon nitride should possess the highest density (0.2957 atom-mol cm⁻³). Such a high density and the topology of bonds in cubic carbon nitride suggest its high heat conductivity. The mechanical stability of cubic carbon nitride under normal and high pressures also follows from the calculations.¹¹

Pseudocubic carbon nitride (in a number of publications, it is this modification that is called cubic) has a structure of the α -CdIn₂Se₄ type.¹¹ It may be classified as a structure resembling zinc blende with one carbon vacancy per cubic cell.¹⁰ The pseudocubic carbon nitride is similar to β -C₃N₄ in that each

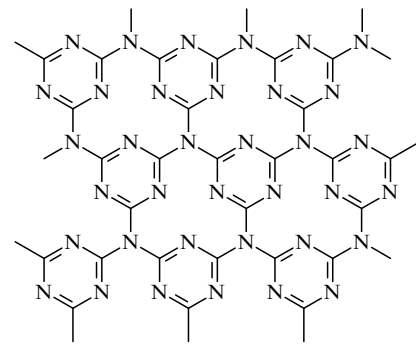


Figure 1. Structure of graphite-like carbon nitride.

carbon atom has four neighbouring nitrogen atoms and each nitrogen atom has three neighbouring carbon atoms. However, the CNC angle in the pseudocubic carbon nitride is close to 109.47°, which is characteristic of *sp*³-hybridisation, and not to 120° characteristic of *sp*²-hybridisation as in β -C₃N₄. β -C₃N₄ was reported^{10, 11} to be somewhat more stable than the pseudocubic form, whereas the opposite result was obtained in another study.¹⁸ This is due to the insufficient accuracy of calculation techniques.

Graphite-like carbon nitride has a layered structure and relates to β -C₃N₄, like graphite relates to diamond. The layer structure is shown in Fig. 1. This ‘perforated’ layer is seen to consist of a series of triazine rings linked through nitrogen bridges. The layers are stacked as ABCABC...,¹⁰ though the ABAB... type is also possible.¹¹ Non-empirical molecular-dynamic calculations have shown that the interlayer distance is 3.07 Å, which is 8% smaller than in graphite and graphite-like boron nitride.¹⁰ For the two-coordinate nitrogen atom (nitrogen in the triazine ring) the bond angle is 116°, and the mean C–N bond length is 1.36 Å, *i.e.* it is close to the sum of Slater radii of carbon and nitrogen.

Similar results were obtained¹⁸ by the method of density functional in the local density approximation for the exchange and correlation functionals. To simplify calculations, it was assumed that all the nitrogen atoms in the system are equivalent, and the corresponding atoms in the neighbouring layers are strictly one under another. The length of the C–N bond was found to be 1.38 Å and the interplanar distance, 3.2 Å. Both values are in good agreement with the above-cited results.¹⁰ The phase transition pressure of graphite-like carbon nitride in the cubic modification is 12 GPa.¹¹ Essentially, the graphite-like carbon nitride is the most stable of all modifications analysed so far. The calculated properties of different phases of carbon nitride are presented in Table 1.

Table 1. Characterisation of different phases of carbon nitride.

Parameter	α -C ₃ N ₄	β -C ₃ N ₄	Cubic C ₃ N ₄	Pseudocubic C ₃ N ₄	Graphite-like C ₃ N ₄	Ref.
Space group	C_{3v}^4 ^a $P3_1c(159)$	C_{6h}^2	$\bar{I}43d(220)$	$P\bar{4}3m$ $P\bar{4}2m(111)$	$R3m$ $P6m2(187)$	9
		$P6_3/m$				20
		$P6_3/m$				10
		C_3^1 ^a				15
Z	4 ^a 4	2 2 ^a 2	4	1	2	8–10
						15
						11
<i>a</i> / Å	6.59 6.35 ^a	6.44		3.43	4.11	9
		6.533				26
		6.41				10
		6.47				21
		6.38				15
		6.35 ^a				15

Таблица 1 (continued).

Parameter	α -C ₃ N ₄	β -C ₃ N ₄	Cubic C ₃ N ₄	Pseudocubic C ₃ N ₄	Graphite-like C ₃ N ₄	Ref.
a /Å	6.4665 6.46	6.4017 6.42	5.3973	3.4232 3.41	4.7240 4.09	11 18
c /Å		2.400 2.45 2.47 2.46 ^a 2.4041			6.7205	26 21 15 15 11
c/a		0.3827 0.375 0.379				20 10 21
Length of C—N bond /Å		1.47 1.45		1.48	1.36 1.38	8, 9, 19 10 19
Interplanar distance /Å					3.07 ~3.2	10 19
Angle C—N—C /degree	~109.47	112–124		108–110	116 ^b	10
Angle M—C—N /degree	115 ^c	108–112				18 10
B /GPa		427 ± 15 437 421 351 189 ^a 425 567	496	425 448 556	51	8, 9 10 21 15 15 11 18
B' /GPa		3.7 5.12 3.3 3.4	3.4	3.4		10 21 11
E_c /eV per monomer unit		40.5 40.75 47.71 41.6 48.9 33.4–35.8		46.56 49.6	47.85	8 9 10 22 18 23
E_0 /eV per monomer unit	–1598.669	–1598.403	–1597.388	–1597.225	–1598.710	11
ρ /g cm ^{–3}	3.45 3.78 ^a 3.58	3.45 3.50 3.56 ^a 3.58	3.89	3.81	2.33	26 15 15 11
ε		3.2				21
Total valence- band width		24.8 24.5 24.8			24.0	9 20 19
Band gap		3.2 3.11 2.1 3.85	2.90			9 20 19 11

Note. The following designations were used: Z is the number of monomers per unit cell; a and c are unit cell parameters; B' is the pressure derivative of the bulk modulus; E_c is the energy of cohesion; E_0 is the total energy; ρ is density; ε is dielectric constant. To unify the data from different publications, the values of bulk modulus are all expressed in GPa, the energy of cohesion, in eV per monomer unit, and density, in g cm^{–3}.

^a Calculations included geometry optimisation. ^b Two-coordinate nitrogen. ^c Pyramidal nitrogen.

In conclusion, let us note briefly some other results of theoretical calculations. The geometric coordinates of atoms in the crystal lattices of carbon nitride were determined.^{10, 11} Electronic and optical properties of β -C₃N₄ and the dependence of optical properties on pressure were estimated in the local

density approximation.²¹ The normalised density functions of β -, pseudocubic, and graphite-like C₃N₄ were calculated.²⁴ Electronic and optical properties of β -C₃N₄ were discussed and an idea of the possible existence of carbon nitride in the form of nanotubes, was suggested.²⁵

III. Carbon–nitrogen films: preparation, properties, formation mechanism

After the pioneering studies of Cohen and Liu,^{6,8} many attempts have been made to materialise their ideas. Most of the studies concerned with the synthesis of crystalline carbon nitride aimed at preparing carbon–nitrogen films. This was by no means the easiest way to obtain carbon nitride (in our view, it is just the opposite), but rather the direction in which, by the beginning of this series of studies, advanced techniques had been developed and rich experience gained in the synthesis of carbon films, including the diamond-like ones.[†]

One of the most common ways for preparing thin films is chemical vapour-phase deposition. In its application to carbon–nitrogen materials, it consists essentially in having the initial substances in their specific forms (atomic, molecular, cluster, or ionised) either existing in, or brought into, the gas phase (by vaporisation, or spray) and forming the target films by interaction on the surface of a specially selected substrate.

As regards the initial substances to be used for the synthesis of carbon nitride, it is natural to rely on its constituent elements, *viz.*, nitrogen and carbon. Nitrogen is used either in pure state or in its mixture with argon. Of the carbon allotrops, graphite is most often used, while diamond and glassy carbon are employed on rarer occasions. The latter is a low-density ($\sim 1.5 \text{ g cm}^{-3}$) non-ordered graphite-like material with a microscopically turbostratic structure consisting of an ordered (local order) network of sp^2 -hybridised carbon atoms.³⁷

As the carbon source for preparing carbon–nitrogen films, various hydrocarbons can be used that, in contrast to graphite, do not require special vaporisation: methane,^{38–44} ethylene,^{45,46} acetylene,^{47,48} cyclohexane,⁴⁷ cyclopentane,⁴⁹ and benzene.^{50,51} Ammonia may well be used as the nitrogen source.^{43,44} However, in all of the above-mentioned cases the resulting films contained considerable amounts of hydrogen, which naturally hampered the identification of carbon nitride in them. It is also noteworthy that even when the initial substances were hydrogen-free, it might be present in films as an admixture.⁵²

In a number of studies specially devoted to the search for carbon nitride, the sources of carbon were hydrogen-containing compounds, such as the already mentioned methane,^{53,54} low-molecular-weight polyethylene,^{55,56} and wax.⁵⁵ Ammonia was used as the nitrogen source;^{54,56–58} incidentally, it was noted⁵⁷ that ammonia was to some extent even more convenient than molecular nitrogen because its chemical bonds are markedly weaker than those in N_2 .

The transfer of carbon to the gas phase and the preparation of chemically active particles necessary for vapour-phase deposition are energy-consuming processes. In the preparation of carbon–nitrogen films, this is achieved in a few ways. Of these, the most popular seems to be magnetron discharge.^{58–76} In yet another method the graphite to be volatilised is used as an electrode to which voltage is applied^{24,58,70,77–84} so that the process is as a rule realised in an electric arc mode. Also rather widespread are the methods of laser ablation of graphite^{85–96} and glassy carbon,⁷¹ graphite vaporisation under the action of an electron beam^{97–100} or a beam of argon ions,^{57,101–103} and radiofrequency diode spraying.^{104–113} A beam of carbon ions was also used to prepare carbon–nitrogen films.^{114,115} The films can also be obtained by pyrolysis (see below).

[†] Furthermore, irrespective of the carbon nitride problem, investigations have continued on the synthesis of carbon films doped with nitrogen to enhance their performance. In this connection no effort was made to introduce the maximum amount of nitrogen in films (it amounted, as a rule, to a few atomic percent and sometimes to percent fractions), and no measurements intended to detect carbon nitride were carried out. Therefore, when citing some recent publications on this topic,^{27–36} we do not discuss them in detail.

In most cases, silicon is used as a substrate on which the process of film formation takes place, see, for example, Refs 53–58, 60–71, 75–78, 80, 83, 85, 87–90, 92, 94–103, 106–108, 111, 113–115. The role of the substrate is also played by sodium chloride,^{56–59,62,72,101} potassium chloride,^{58,70} glass,^{24,59,91,94,104,106,107,109,110,113} quartz,^{98,113} potassium bromide,^{106,110,112} glassy carbon,^{62,107,110} sapphire,^{72,74,100} mica,^{58,83} copper,^{102,115} gold,¹¹⁵ beryllium,¹⁰² magnesium,¹¹⁵ zirconium,^{59,60,75} germanium,¹⁰⁸ tantalum,^{114,115} molybdenum,^{114,115} tungsten,¹¹⁵ nickel,^{79,85} steel,^{66,67,73,81} tungsten carbide,^{97,98} cemented carbides,⁶⁷ and a NiP/AlMg system.¹⁰⁵ Alkali metal halides are convenient as substrates because they are readily soluble in water, which facilitates the isolation of films in a pure state. As regards mica, it was noted⁵⁸ that some of its lattice parameters are close to those of $\beta\text{-C}_3\text{N}_4$.

Yet another method for the preparation of carbon–nitrogen films is based on ionic implantation. It differs from the methods listed above in that the carbon itself is bombarded with an ionic nitrogen beam and is the substrate on which a film is formed. The corresponding beam is usually generated by an ion gun. Various carbon modifications may be used as substrates: graphite,^{115–121} diamond,^{121,122} glassy carbon.^{24,37,123}

The properties of carbon–nitrogen films were studied in detail. We shall give special attention to the properties that are directly related to the problem of carbon nitride preparation. In this context, two questions seem to be of prime importance: how much nitrogen is incorporated into films and whether these films have a crystalline phase.

Before proceeding to the consideration of the respective data, note that the properties of carbon–nitrogen films depend substantially on both the method of synthesis and the parameters of the process. Therefore, the results reported by different authors differ noticeably.

The concentration of nitrogen in films was determined by the electron energy loss spectroscopy, Rutherford backscattering, Auger electron spectroscopy, *etc.* The content of nitrogen in films varied over a wide range.

Nitrogen content (at. %)	Ref.
20	37, 55, 75, 83, 95, 117, 118, 121
20–30	24, 64, 69, 76, 78, 82, 87, 94, 104, 106, 123
30–40	56, 57, 61, 62, 65, 70, 71, 73, 74, 80, 81, 88, 90, 91
40–50	54, 58–60, 85, 86, 92, 96, 99–101, 103, 105, 107–110, 114, 115, 124

There are only a few papers reporting the contents of nitrogen in films approaching the value of 57.1 at.% corresponding to C_3N_4 : 58,⁵³ 54.6,⁶⁸ 57,^{72,102,111} 83 at.%.⁹⁷ Note that the nitrogen level of 58% was determined disregarding the hydrogen content in the film; furthermore, the accuracy of measurement was 20%. The reason for an anomalously high value of 83 at.% is unclear. The only thing to be mentioned in this connection is that the distribution of nitrogen in the films is far from being always regular: its concentration on the film surface was repeatedly noticed to be higher than inside the film.⁸³ In particular, this may be due to the fact that not all the nitrogen contained in the film is chemically bound. Thus, in a study¹²² unrelated to the problem of carbon nitride synthesis, it was noted that the surface concentration of nitrogen in the film prepared by the bombardment of diamond with nitrogen ions may be as high as 81 at.%, while at a depth of 20 Å it is twice as low. One should bear in mind that all of the above-cited nitrogen concentrations represent the mean values. Therefore, one should not rule out the possibility that even in films with low nitrogen levels its local concentrations may exceed considerably the mean value. Thus it was found¹⁰¹ that at the mean nitrogen concentration of 45 at.% its local level may achieve 59 at.%.

X-Ray and electron diffraction studies were undertaken to detect crystalline phases in carbon–nitrogen films. Some films proved to be totally amorphous,^{24, 62, 71, 72, 74, 77, 80, 83, 91, 98, 113} whereas crystallites were also detected in a background of predominantly amorphous phase, see *e.g.* Refs 54–61, 64, 71, 78, 85–90, 99, 102, 104, 107–109, 112, 114, which were attributed directly to β -C₃N₄ on the basis of diffraction measurement results.^{56, 75, 78, 85, 86, 88–90, 99, 102, 108, 109, 112, 114, 119} The formation of β -C₃N₄ was also confirmed by the results of X-ray photoelectron,⁷⁵ Raman,⁷⁸ and IR spectroscopy.⁵⁵ Crystallites proved to vary in size: from very small, not exceeding 10 nm,^{58, 60, 61, 64, 85, 86} to markedly larger with a size of 100 nm,^{59, 102} and even up to 0.4 μ m (see Ref. 99) and 0.5 μ m.¹⁰⁸ Needle-shaped crystallites 300 nm in size were obtained.⁵⁴ Their diffraction pattern was found to be similar to that of α -C₃N₄, while β -C₃N₄ was not detected. As a result of laser-induced microbursts at the interface of frozen ethanol and liquid nitrogen layers, microcrystals up to 100 μ m in size were obtained;⁷¹ however, their composition was not established.

Despite the fact that in some of the above-cited studies fairly definite conclusions on the existence of C₃N₄ crystallites in carbon–nitrogen films have been made, they nonetheless should be considered with caution. These films have complex structures, they may include different phases, and finally, they often contain admixtures of other elements (hydrogen, oxygen, *etc.*) affecting the results of measurements. For example, it was noted¹²⁵ that some data on electron diffraction in such films are closer to the analogous data for the carbon phase of lonsdelite than to C₃N₄. In this context, one should agree with the arguments of Fang¹²⁶ that the available evidence of the formation of crystalline carbon nitride is rather ambiguous.

Let us analyse other properties of carbon–nitrogen films. Numerous measurements of the thickness of such films^{53, 55–58, 61, 63, 66, 69, 72, 74, 75, 81, 83, 84, 92, 94, 96–100, 105–107, 110, 115} show that it varies within wide limits ranging from tens of angstroms⁵³ to micrometers. The thickest films were 2 μ m (Ref. 66) and 3.9 μ m (Ref. 74). A film separated from the substrate (by dissolving NaCl) was found to be 50 nm thick.⁷²

Undoubtedly, the formation of films involves chemical bond formation between carbon and nitrogen. This was confirmed by X-ray photoelectron spectroscopy;^{53–57, 71, 76, 84, 85, 88–90, 97–99, 101, 103, 105, 106, 114, 116–119, 122} in some cases, certain information was obtained on the character of the bonds formed. Thus the formation of weakly polarised carbon–nitrogen bonds characteristic of C₃N₄ was established.^{55–57, 90} It was also shown that the hybridisation of carbon may be sp^2 and sp^3 .^{57, 75, 99, 101, 105} In general, judging from the X-ray photoelectron spectra, the composition of carbon–nitrogen films is rather complex and may include various functional groups.^{37, 77, 117, 121}

Carbon–nitrogen films were analysed in detail by vibrational spectroscopy. One of the most characteristic features of the IR spectra of these films is the presence of a band at 2200 cm^{-1} attributed to the nitrile group ($\text{C}\equiv\text{N}$).^{24, 55, 59, 62, 63, 68, 70, 77, 87, 91, 92, 94–96, 98, 106, 109, 111–113} Analogous results were obtained by employing Raman spectroscopy.^{60, 73, 81, 82, 84, 89, 90, 95, 109} The formation of nitrile groups was also confirmed by X-ray photoelectron spectroscopy.^{37, 55, 65, 90, 98, 121, 122}

The fact that the nitrile groups are present in films obtained by different methods and under different conditions (in particular, the $\text{C}\equiv\text{N}$ group is virtually always observed in the IR spectra) makes it possible to conclude that the formation of nitrile groups is a common phenomenon in the preparation of carbon–nitrogen films. However the nitrile group was considered as an admixture,^{92, 96, 127} though it appears to be an admixture in relation to a hypothetical carbon nitride.

The formation of nitriles in the interaction of carbon with nitrogen is not surprising because of the strength and energetic

advantage of the triple carbon–nitrogen bonds. The high strength of this bond ensures its stability under drastic conditions of film formation (high temperatures, large energies of nitrogen and carbon ions).

It is difficult to characterise nitriles in the carbon–nitrogen films. It is possible that these compounds are of the paracyanogen type, which is a polymer with a complex branched structure.¹²⁸ It contains $\text{C}\equiv\text{N}$ and $\text{C}=\text{N}$ bonds. It is noteworthy that, according to the spectral data, the formation of $\text{C}=\text{N}$ bonds in the carbon–nitrogen films is quite possible.^{53, 65, 68} It is also noteworthy that in 1979, when the problem of carbon nitride synthesis was not yet adequately formulated, paracyanogen was prepared by the method of reactive radiofrequency sputtering,¹²⁹ which was subsequently often used for the synthesis of carbon nitride. It was also pointed out^{72, 90, 130} that paracyanogen structures can be formed in the carbon–nitrogen films. It was found⁹⁶ that nitriles can be removed from the film by annealing. After annealing, a material corresponding in its composition to C₂N was obtained. This does not contradict the above-mentioned high strength of the $\text{C}\equiv\text{N}$ bond and can be explained by the destruction of nitrile-containing compounds (including paracyanogen) upon prolonged heating without cleavage of the triple bonds.

To conclude the review of nitriles in carbon–nitrogen films, we can mention a study,⁸⁰ which suggested the formation in carbon–nitrogen films of a nitrile compound called polycyanimine, which was found to be rather similar to paracyanogen in structure.

The application of vibrational spectroscopy has revealed yet another phase often occurring in the carbon–nitrogen films. In the IR spectra of films obtained by different methods, three commonly occurring peaks were repeatedly found at 1500, 1300, and 700 cm^{-1} .^{62, 87, 94, 109, 112} Analogous bands were observed at 1500 and 1300 cm^{-1} in the Raman spectra.^{37, 60, 71, 81, 86, 90, 95, 109, 120, 131} The first of them (*G*-branch) is ascribed to graphite-like carbon, the second band (*D*-branch) was attributed to non-ordered carbon, whereas the band at 700 cm^{-1} was ascribed to the extraplanar deformational vibrations of graphite-like regions (in all cases, the carbon atoms are in sp^2 -hybridisation). It is important that for symmetry reasons all of these vibrations must be active in the Raman spectra and inactive in the IR spectra. However, the substitution of a few carbon atoms by nitrogen atoms in the graphite rings results in symmetry perturbation and the corresponding vibrations become IR-active. Thus, the carbon–nitrogen films are believed to include graphite-like structures in which some carbon atoms are replaced by nitrogen atoms. This is supported by NMR data.⁶³ It was suggested that compounds of the composition C₂N and C₅N⁶³ can be formed, as well as compounds in which one nitrogen atom is linked with three carbon atoms.²⁴ The possibility of the existence of the above-mentioned graphite-like nitrogen-containing compounds has been long known. For example, they can be prepared by pyrolysis of polyacrylonitrile incorporated into urea.¹³²

Interesting ideas were expressed by Sjöström *et al.*^{69, 76} on the basis of data from quantum mechanics calculations, X-ray photoelectron spectroscopy, and electron microscopy: it was concluded that the sp^2 -hybridised graphite-like carbon–nitrogen planes are bent and cross-linked by sp^3 -hybridised bonds. It is important that the bend of the plane is due to the incorporation of five-membered rings, *i.e.* a fullerene-like carbon–nitrogen structure appears.

Crystalline carbon nitride has been supposed to have high hardness since the very first studies; therefore, it was natural to check this with the carbon–nitrogen films. One could not expect a record hardness because of complex film composition, though the possibility of preparing films with good performance was not ruled out. In practice, it proved to be the case. Mechanical characteristics of films (hardness, elasticity modulus, elastic recovery, friction coefficient, adhesion) were studied in numerous studies.^{55, 57, 59, 60, 64, 66, 69–71, 73, 74, 76, 81–87, 89, 90, 97, 98, 103, 113} As a result, it was found that carbon–nitrogen films possess high hardness, large elastic recovery, good adhesion to different

materials (primarily, to silicon), and some other valuable properties. For instance, on the surface of titanium nitride the hardness of a carbon–nitrogen film corresponds to that of diamond and is higher than that of cubic boron nitride.⁶⁶ The elastic recovery of films amounts to 84%–85%.^{64,76} In the indentation of films, microcracks (as in titanium nitride) are not formed, and plastic deformation occurs instead. On the surface of titanium carbide the film hardness reaches 6500 kg mm⁻² on Knoop's scale (see Ref. 97). As noted by the authors, no films of such hardness with a thickness of 1 mm have been obtained previously.

The density of films was measured in a number of studies, it was found to be 2.2 and 2.30 g cm⁻³ (see Refs. 59, 65, respectively). A film with a density of 3.4 g cm⁻³ was prepared¹⁰² which is close to the theoretical value of 3.47 g cm⁻³ for β -C₃N₄.

Some other properties of carbon–nitrogen films were also studied. Since they are not of direct relevance to the problem of carbon nitride synthesis, we shall make only a brief mention of them. In a study,¹¹³ the EPR method was employed to study paramagnetic properties of films. The spin density was found to vary from 1.1×10^{18} to 1.1×10^{19} cm⁻³. It was concluded that the EPR-active centres are localised on carbon atoms. They were attributed to the unordered phase with *sp*²-hybridised carbon. The nitrogen contained in the film decreases the concentration of this phase and possibly increases the concentration of the phase with *sp*²-hybridised carbon.

Studies^{58–60, 80, 87, 91, 94, 96, 106, 113} were concerned with the determination and analysis of the electrical conductivity of C–N films, and their optical properties (refractive index, reflection factor, extinction coefficient, width of optical band gap) were also studied.^{70, 73, 80, 87, 91, 94, 98, 104, 113} These films were characterised by high heat conductivity⁹⁶ (note that this property had been predicted theoretically). In some cases, the thermal stability was assessed. The films remain stable for 30 min at 350 °C,⁶³ they can withstand heating up to 800 °C.⁸⁵

Detailed studies of the properties of carbon–nitrogen films have predetermined discussion, in a number of reports, of their performance and prospects of practical uses. There are indications of the possibility of their application as semiconductors with a variable band gap⁶¹ and wear-resistant coatings.^{61, 87} Such films were reported¹⁰⁵ to be suitable as protective coatings in systems of magnetic registration. In this respect, they are superior to the purely carbon films.

Information about processes occurring during the film formation is very scarce. As a matter of fact, one can speak only about the type of particles involved in these processes.

As the nitrogen interacting with carbon has been subjected previously to energy impact (radiofrequency discharge, electric arc, electron cyclotron resonance, laser radiation, *etc.*), it was always in the ionised or atomic state, the proportion of different active particles being dependent on experimental conditions. Thus, in experiments on ionic implantation, the nitrogen ions had an energy of 160 keV;¹²³ in analogous experiments^{37, 118, 121} an ion gun produced N₂⁺ ions with an energy of 500 eV, whereas the plasma of electron cyclotron resonance yielded low-energy nitrogen ions with an energy of 20–30 eV.¹⁰⁰ In another study⁶⁵ ion beams comprised atomic nitrogen and N⁺ ions, the latter present in amounts from 2.5% to 25%;⁶⁵ or 80% of N₂⁺,¹⁰² or 96% of N₂⁺ and 4% of N⁺.¹¹⁶

Carbon also exists in the ionised or atomised state in the process of film formation. The use of beams of C⁺ was reported.^{114, 115} Evaporation in an electric arc leads to the formation of carbon atoms and clusters, as well as C⁺, C₂⁺, and electrons.^{58, 82} In experiments on laser ablation of graphite, atomic carbon, C₂, and other carbon clusters were formed.⁸⁹ Irrespective of the problem of carbon nitride synthesis, laser vaporisation of graphite was studied;¹³³ it was shown that atomic carbon, as well as C₂, C₃, and C₄ clusters were formed.

The plasma over substrate contained not only carbon and nitrogen. The formation of CN radicals is also possible.⁷⁷ The

presence of these particles in the reaction system is important for the understanding of the formation of the above-mentioned nitriles.

Numerous studies were concerned with the measurement of the rates of the film growth.^{53, 55–60, 62, 64–66, 68, 70, 71, 74, 75, 81, 84, 88, 92, 96, 99, 100, 105, 107, 113} It was found to vary from 1 Å min⁻¹ (see Ref. 53) to 5 nm s⁻¹ (see Ref. 64). The growth rate is an important characteristic of both the yield and the mechanism of the process. It was shown^{93, 96} that the film growth rate determines the nitrogen content in it. It follows that the key stage of the film growth is not the process in the gas phase, but rather the reaction between carbon and nitrogen on the growing surface. This reaction may be preceded by the dissociation of N₂⁺ upon its collision with the surface.^{102, 118}

Summarising the above considerations, it may be stated that the carbon–nitrogen films possess a number of valuable characteristics and are of obvious practical interest. As regards the possibility of preparation of crystalline carbon nitride by non-pyrolytic film formation (in particular, in the form of an individual substance and not as a microphase), we are rather pessimistic despite some progress in this direction. In our view, the major difficulty lies in that the energy of the particles used in the process of film preparation exceeds considerably that of the chemical bonds in the hypothetical carbon nitride. Even when low-energy nitrogen atoms are used, their energy is 20–30 eV, while the strongest chemical bonds have a dissociation energy of 10 eV, and in the case carbon nitride it does not exceed 4 eV (judging from the cohesion energy level, see Table 1). If one uses higher-energy particles, the corresponding energies differ by orders of magnitude. The high energy of the particles involved in the reaction to promote a high rate of the process means that the time for the energy to dissipate is then too short, and the energy is spent in the cleavage of the newly formed C–N bonds. Nonetheless, some bonds have enough time to form, though in the light of what has been said above, the conditions are more favourable for the formation of stronger double and triple bonds, rather than of single C–N bonds, as in carbon nitride, and this was indeed observed experimentally. Apparently, for the same reason even when carbon nitride crystallites are formed, they are very small.

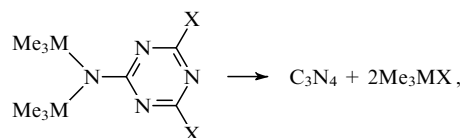
IV. Pyrolysis

Pyrolytic processes underlie the synthesis of numerous materials; therefore, their use for the preparation of carbon nitride appears quite natural. Clearly, it is preferable to use high-nitrogen substances as precursors of carbon nitride. Depending on the conditions of the process, the final product may be obtained in the form of a voluminous mass (*e.g.*, a powder) or as a thin film. The latter case was realised¹³⁴ in the pyrolysis of 3,3'-diaminobenzidine and melamine. The corresponding reactions lasted for 1 h at 800 °C (heating to 800 °C was accomplished at a rate of 10 °C min⁻¹). The decomposition products of the above-mentioned substances contained 11.7 mass% and 39 mass% of nitrogen, respectively, and small quantities of hydrogen (0.8 mass% and 2 mass%). The volatile products of the reaction were nitrogen, ammonia, and hydrogen cyanide. This study¹³⁴ was not concerned with carbon nitride synthesis, therefore it is not discussed at all. However, this task was already in view in the next study by the same authors.¹³⁵ In this case, melamine, 1,2,4-triazole, diaminomaleonitrile, polymerised hydrogen cyanide, dicyanoimidazole, tetracyanoethylene, its mixture with ammonia, and hexaazatriphenylenehexacarbonitrile were subjected to pyrolysis. The reactions were also conducted at 800 °C and yielded a solid residue containing from 25 mass% to 45 mass% of nitrogen.

However, this attempt to prepare carbon nitride failed: the results of X-ray analysis indicated that the product was amorphous, while its pycnometric density was 1.71 g cm³, which is considerably less than the theoretical value for β -C₃N₄. Judging

by the results of Raman spectroscopy and ^{13}C NMR, the carbon in the synthetic product is in the sp^2 - and not in sp^3 - hybridisation, while the product itself seems to have a characteristic graphite-like structure in which certain carbon atoms are replaced by nitrogen.

Pyrolysis of triazine derivatives gave interesting results.^{136, 137} The reactions proceeded according to the scheme:



where X is chlorine or fluorine and M is silicon¹³⁶ or tin.¹³⁷

The process may be regarded as a condensation in which the group Me_3M of one molecule of the substrate interacts with X of another molecule. This results in the elimination of the corresponding silane or stannane, while two triazine rings are linked by a nitrogen bridge. This linkage should lead to the appearance of the structure shown in Fig. 1 and theoretically predicted for the graphite-like carbon nitride (see above). The presence of such structure was confirmed by spectral measurements.^{136, 137} Unfortunately, the product obtained in these studies proved to be amorphous. Thermolysis was conducted at 400–500 °C, the tin derivative being thermally less stable than that of silicon. The products were obtained as films up to 0.5 μm thick. The deposition rate achieved was 300 $\text{\AA min}^{-1}$. The tin derivative (but not that of silicon) could also be obtained as a powder when the reaction was carried out at 200 °C. Depending on the experimental conditions, the product included small quantities of admixtures. Thus, the pyrolysis of the silicon derivative yielded a film of the composition $\text{C}_3\text{N}_4\text{O}_{0.3}\text{Si}_{0.02}\text{F}_{0.05}$. The authors^{136, 137} were correct in pointing out that the material they had prepared might prove to be a convenient precursor for the synthesis of crystalline carbon nitride (at least, graphite-like). The reason for the optimism is not only the stoichiometric composition of the product, but also that, in contrast to other carbon nitride precursors, it contains only C–N bonds (with no account of admixtures).

Combined pyrolysis of pyridine and chlorine at 800 °C yielded a product of approximate stoichiometry of C_5N .¹³⁸ Judging by the results of electron diffraction, it has a layered structure, and it is not ruled out that, as in a number of cases considered above, this is a graphite-like product in which some (one out of six) carbon atoms are replaced by nitrogen.

In conclusion, a study can be mentioned¹³⁹ in which the process was not thermal in character and the product was not a film. Etching of diamond or graphite with a microwave nitrogen plasma produced a soft porous low-density carbon–nitrogen material of a structure similar to the turbostratic structure of graphite or the hexagonal structure of boron nitride. This material decomposes at 900 °C or even at lower temperatures.

V. High pressure

The synthesis of numerous carbon materials (including that of diamond) is carried out under high pressure, and it seems natural that higher pressures would favour the preparation of carbon nitride. The expedience of high pressures for the synthesis of carbon nitride was pointed out in a number of papers (see, e.g., Refs 9, 11, 135).

Pyrolysis of 1,3,5-triazine and tetracyanoethylene was carried out at a temperature of 1400 °C and a pressure of 5 GPa, and reaction lasted for 30 min.¹⁴⁰ The product of triazine pyrolysis was found to contain no nitrogen whatsoever, while pyrolysis of tetracyanoethylene yielded a graphite-like material of composition $\text{C}_{4.66}\text{N}$. Judging from electron energy loss spectroscopy, the carbon contained in this product was exclusively in sp^2 -hybridisation. Apparently, as in a number of cases considered above, pyrolysis of tetracyanoethylene yielded a graphite-like product in which some of the carbon atoms were replaced by nitrogen.

Other authors¹³⁵ described low- and high-pressure pyrolysis (225 MPa) of hexaazatriphenylhexacarbonitrile and tetracyanoethylene for 70 h at 700 °C. However, in this case, too, amorphous products were obtained with nitrogen contents of 36.1 mass % and 39.3 mass %, respectively. Incidentally, it was noted that these products (having the same structure as the low-pressure pyrolysis products) may be convenient precursors for the synthesis of carbon nitride.

Pyrolysis of paracyanogen for 75 h at 725 °C and 0.3 GPa yielded graphite-like carbon as the sole product.¹²⁸ The authors noted that paracyanogen is inconvenient for the carbon nitride synthesis because it can undergo decomposition at relatively low temperatures.

As far as we know, there is only one instance of the use of the method of shock-wave compression for carbon nitride synthesis.²⁶ The product of pyrolysis of melaminoformaldehyde resin and the products of low-temperature combustion of tetrazole and its sodium salt were the objects for the shock impact. These materials were compressed by shock under the conditions typical of the synthesis of diamond and wurtzite-like boron nitride, where the pressure seemed to reach 60–250 GPa. However, no carbon nitride was obtained; instead diamond was detected the structure of which proved to be much more ordered than that of diamond prepared from carbonaceous precursors. It is believed¹³⁹ that the reason for unsuccessful attempts²⁶ to obtain carbon nitride was the presence of hydrogen in the original reagents. The expedience of the use of hydrogen-free compounds was also pointed out in Ref. 135. In our opinion, this is not the only reason. Other reasons will be considered below.

We have already demonstrated that in various attempts to synthesise carbon nitride the final product contained, as a rule, nitrogen at levels below the required 57.1 at.%. In order to overcome this deficit, it was recommended¹⁴¹ to use lithium azide (or other metal azide) as the nitrogen source and to subject its mixture with a non-diamond form of carbon to shock-wave compression under a pressure of about 100 kbar. As a control, it was proposed to conduct the experiment so as to provide for the synthesis of carbon nitride in one part of the reactor and, in another part separated from the first one, for the analogous synthesis of silicon nitride (the synthesis may also be carried out in a single mixture). This may permit obtaining additionally a new phase of silicon nitride (boron may also be added to the system to obtain the 'elusive' BCN phase). The proposed approach is substantiated by the fact that the shock-wave compression of a mixture of boron with lithium azide allows the synthesis of cubic boron nitride.

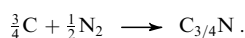
Interesting results were reported¹⁴² on a reaction of carbon with nitrogen. It was carried out at 2000–2500 K and a pressure of 30 ± 5 GPa. The carbon sources were graphite, amorphous carbon, and fullerene C_{60} . This resulted in the formation of a crystalline phase with cubic symmetry. The X-ray diffraction pattern of this phase does not correspond to that for $\beta\text{-C}_3\text{N}_4$, though the very fact of preparation of a crystalline carbon–nitrogen phase is remarkable.

VI. Thermodynamics

The scarcity of our knowledge about the range of thermodynamic stability of carbon nitride determines largely the fact that until now attempts to synthesise crystalline carbon nitride, in particular in the pyrolytic mode, have been unsuccessful. Hence, it is still unclear what process parameters (temperature, pressure) should be 'aimed at' to ensure successful synthesis. Despite the evident topicality of the thermodynamic analysis of conditions of the carbon nitride synthesis, only few studies were concerned with this problem.

Having analysed the available data on the dissociation energies of single C–N bonds ($286\text{--}305 \text{ kJ mol}^{-1}$), the authors²³ assumed that the cohesion energy of carbon nitride should be $E_c = 858\text{--}915 \text{ kJ (mol C}_3\text{N}_4)^{-1}$. As noted above, the repulsion

of unshared electron pairs of nitrogen should make a noticeable contribution to the energy of a carbon nitride crystal.¹⁴ Taking into account this repulsion, one obtains a more accurate range of cohesion energy values, $E_c = 806\text{--}863 \text{ kJ (mol C}_3\text{N}_4)^{-1}$. The cohesion energy is directly related to the thermal effect of the reaction.



Thermodynamic analysis of this reaction allows calculation of the standard enthalpy of carbon nitride formation. It was found²³ that $\Delta H_f^\circ = 147\text{--}204 \text{ kJ (monomer unit C}_3\text{N}_4)^{-1}$. The entropy of C_3N_4 was calculated using the Latimer rule and amounted to $19 \text{ J (K mol C}_3\text{N}_4)^{-1}$, i.e. $77 \text{ J (K monomer unit C}_3\text{N}_4)^{-1}$. Thus, $\Delta S_f^\circ = -78 \text{ J (K mol C}_3\text{N}_4)^{-1}$; $T\Delta S^\circ = -23 \text{ kJ (mol C}_3\text{N}_4)^{-1}$ at 298 K ; and $\Delta G_f^\circ = 171\text{--}227 \text{ kJ (mol C}_3\text{N}_4)^{-1}$.

Knowledge of the thermodynamic properties of carbon nitride made it possible to follow the dependence of the thermodynamic potential of its formation on pressure.²³ This was done with the aid of the Gibbs–Duhem equation using the Birch–Murnaghan equation of state. As a result, the dependences of the specific volume of carbon nitride on pressure were determined for isothermal conditions (298 K).²³ In a thermodynamically unfavourable case [$\Delta G_f^\circ = 227 \text{ kJ (mol C}_3\text{N}_4)^{-1}$ under normal pressure], $\Delta G_f^\circ = 0$ (i.e. the reaction becomes possible) under a pressure of 150 GPa , and at 75 GPa in the optimal case [$\Delta G_f^\circ = 171 \text{ kJ (mol C}_3\text{N}_4)^{-1}$]. One should also bear in mind that to permit the reaction at a sufficient rate (it is short conversion times in the shock-wave compression that could be the reason for failure to synthesise carbon nitride²⁶) rather high temperatures are required and this necessitates increased pressure. Thus in synthesis at 1300 K (this temperature is characteristic of the high-pressure synthesis of diamond) it is necessary to increase pressure by another 30 GPa to make the reaction possible. Such pressures are considerably higher than those realised in the attempts to synthesise carbon nitride (except for the shock-wave compression). Nonetheless, it was noted²³ that since nowadays static pressures up to 200 GPa are achievable, the potential possibility of carbon nitride synthesis is preserved. Thermodynamic analysis of carbon nitride with stoichiometry C_4N_3 which contains some C–C bonds besides the C–N bonds, has been carried out.²³

Thermodynamic analysis of the temperature dependence of the pressure of $\beta\text{-C}_3\text{N}_4$ formation in a system containing solely carbon and nitrogen was carried out.²² In the estimation of the standard enthalpy of carbon nitride formation, it was assumed (based on the equality of bond lengths) that the dissociation energy of its C–N bonds is the same as in methylamine, viz., 80 kcal mol^{-1} . As a result, the enthalpy of $\beta\text{-C}_3\text{N}_4$ formation was found to be $18.6 \text{ kJ (monomer unit C}_3\text{N}_4)^{-1}$ which is much less than the values used in Ref. 23. The results of calculation are shown in Fig. 2. These were used for elucidating the possibility of carbon nitride synthesis through detonation of explosives. It is known that the detonation may lead to the formation of diamond but not carbon nitride because the pressure of detonation products is considerably lower than the pressure of carbon nitride condensation. Possibly, it is this that was the reason that diamond rather than carbon nitride was formed under the shock-wave compression of a number of substrates.²⁶

Yet another approach to the synthesis of carbon nitride has been analysed.²² It is based on adiabatic explosion with subsequent isochoric cooling of the products formed. It was found that with isochoric cooling the system shifted first to the area of thermodynamic stability of diamond and then to that of carbon nitride. Thus, under the conditions considered carbon nitride should be formed through vaporisation of carbon from diamond and condensation of the vapour formed with nitrogen.

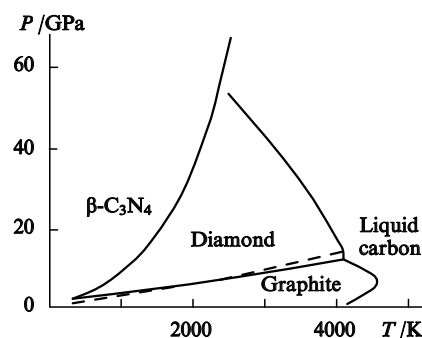


Figure 2. The line of $\beta\text{-C}_3\text{N}_4$ condensation in the carbon phase diagram according to Bundy.¹⁴³

The dashed line shows the calculated graphite–diamond equilibrium.¹⁴⁴

VII. Conclusion

The properties predicted theoretically for crystalline carbon nitride make this product highly attractive. In our view, the actual situation with carbon nitride is similar to that in which the phenomenon of high-temperature superconductivity was a few years ago and the problem of synthetic diamond several decades ago: there are no theoretical restrictions, but experimental efforts fail until a certain stage is reached. The major difficulties seem to be associated with insufficient knowledge of the optimum conditions of carbon nitride synthesis and with the possibility of occurrence of numerous competitive processes leading to the formation of various carbon phases and C–N compounds that are more stable thermodynamically than carbon nitride under given conditions. Nonetheless, the material discussed above enables one to feel optimistic about the synthesis of crystalline carbon nitride. In this review, we touched only briefly upon the possibility of synthesis of a carbon nitride with stoichiometry different from C_3N_4 . However, such a possibility does exist and should be taken into account in relevant studies.

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^b — *Russ. J. Chem. Phys. (Engl. Transl.)*

Skeletal transformations of heterocage compounds involving the hetero-function

B M Lerman

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Abstract. Published data on the skeletal transformations of oxa-, aza-, bora- and polythia-cage compounds accompanied by replacement of one heteroatom by another, of a heteroatom by a carbon atom or of a carbon atom by a heteroatom are surveyed. Skeletal transformations of compounds with oxacage structures leading to compounds with carbocage structures are considered. The bibliography includes 65 references.

I. Introduction

Synthetic methods based on skeletal rearrangements occupy a prominent place in the chemistry of cage and heterocage compounds. The types of these rearrangements are quite diverse; rearrangements typical of cage compounds do not necessarily occur in their hetero-analogues. The most famous skeletal rearrangement of carbopolycyclanes, namely, the thermodynamically controlled isomerisation induced by strong Lewis acids, the discovery of which has opened up the way to adamantane, its homologues, polymantanes and many other cage compounds, provides an example of 'non-universal' processes. This rearrangement has found no use in the synthesis of heteroorganic derivatives, because their skeletons are unstable in strongly acidic media. However, a large number of rearrangements occur successfully in reactions of both cage and heterocage compounds. This group includes the rearrangement of (hetero)cubanes into (hetero)snowtanes, photoisomerisation of (hetero)polycyclodienes, skeletal interconversions of functionally substituted (2,4,6,8-tetrathia)adamantanes and (2,4,6,8-tetrathia)protoadamantanes, *etc.* These rearrangements have been considered in the monographs by Fort¹ and Bagrii,² in the well known reviews dealing with the chemistry of cage and heterocage compounds^{3–5} and in a number of reviews specially devoted to skeletal rearrangements of this type of compound.^{6–9}

In addition to rearrangements that are common to cage compounds and their hetero-analogues and to those peculiar only to cage compounds, there exist skeletal rearrangements, which are typical only of heterocage derivatives, because they

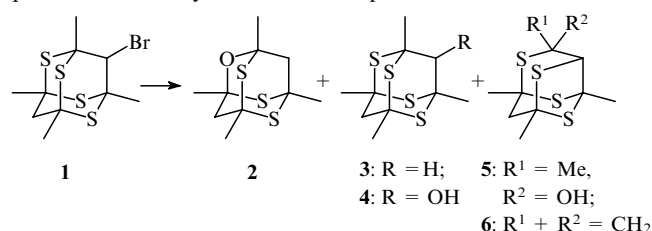
involve the hetero-function. The picture of skeletal rearrangements of (hetero)cage compounds is not complete without this type of rearrangements. However, they have not been considered in the monographs and reviews mentioned above. The purpose of the present review is to fill this gap. We survey the available data on the skeletal transformations of functionally substituted heteropolycyclanes in which a heteroatom is replaced by another heteroatom or by a carbon atom, or a carbon atom is replaced by a heteroatom, the initial heteroanalogous framework being retained. The skeletal rearrangements of oxacage compounds giving rise to derivatives with a related oxacage or a stabilomer carbocage structure are also considered.

II. Skeletal transformations with replacement of one heteroatom by another

Transformations of this type accompany some reactions of functional derivatives of 1,3,5,7-tetramethyl-2,4,6,8-tetrathiaadamantane and compounds with the 'bird-cage' structure containing a heteroatom, *i.e.* with the structure of 4-heterohexacyclo-[5.4.1.0^{2,6}.0^{3,10}.0^{5,9}.0^{8,11}]dodecane. These transformations give rise to compounds with the same cage structure but with a different heteroatom. Some functional derivatives of the 'bird-cage' series isomerise under the action of appropriate reagents. The initial number of heteroatoms in the cage as well as the initial carboanalogous structure are retained in all the transformations under consideration.

1. S → O transformations

Solvolysis of 9-bromo-1,3,5,7-tetramethyl-2,4,6,8-tetrathiaadamantane **1** in 50%–92% aqueous acetic acid affords a debromination product, 2-oxa-4,6,8-trithiaadamantane **2** with a different system of heteroatoms. In addition to **2**, the reaction yields a number of compounds in which the initial structure is retained, namely, debromination product **3** and solvolysis product **4**, and derivatives with the protoisomer structure, namely, hydrolysis product **5** and dehydrobromination product **6**.



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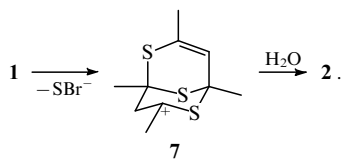
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The proportion of the compound **2** in the product mixture depends on the concentration of acetic acid, the highest content (56%) being attained in 90% acid (Table 1). It is noteworthy that solvolysis of the bromide **1** in 50%–90% formic acid also yields **2**; however, in this case, the proportion of **2** in the product mixture does not exceed 5%.^{10,11}

Table 1. Acid solvolysis of the bromide **1** under various conditions.

Acid concentration (%)	Composition of the reaction products (%)			
	2	3	4	5, 6
MeCOOH				
92	54	37	9	—
90	56	34	6	—
80	40	34	26	—
70	18	46	33	—
60	10	42	27	18
50	2	22	15	45
HCOOH				
92	2	37	62	—
85	5	37	58	—
60	4	37	59	—
50	2	36	55	—

A probable scheme for this transformation includes fragmentation with the abstraction of SBr^- and subsequent cyclisation of the unsaturated bicyclic intermediate **7** induced by H_2O and leading to the incorporation of oxygen into the skeleton.



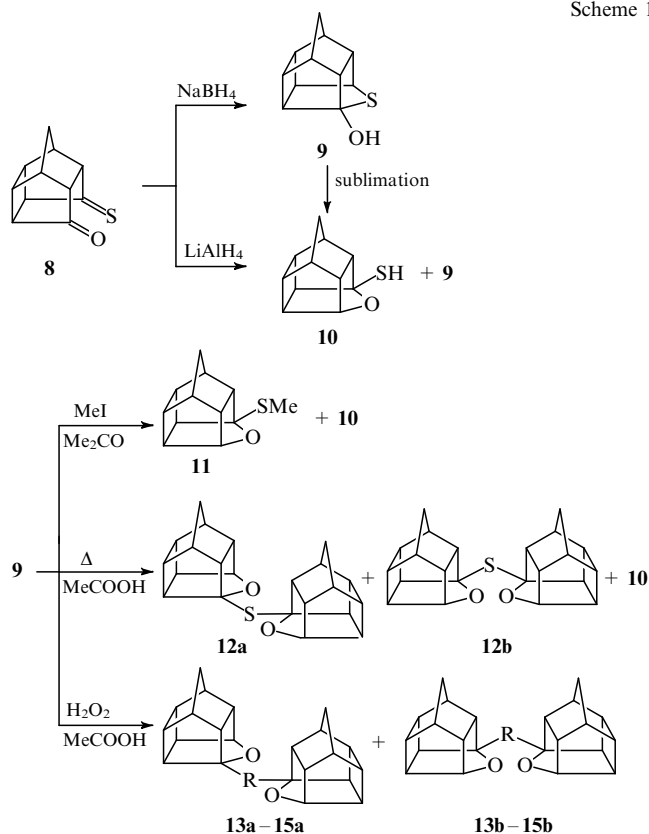
It should be noted that the compound **2** is formed as a side product in the synthesis of 1,3,5,7-tetramethyl-2,4,6,8-tetrathiaadamantane **3** by condensation of acetylacetone with hydrogen sulfide in concentrated HCl. Condensation of these compounds in glacial acetic acid affords **3** as the only product.¹²

Transformations of 4-hydroxy-derivative **9** are also accompanied by skeletal rearrangements in which the sulfur atom is replaced by oxygen (Scheme 1). The compound **9** is prepared from thioketone **8** having a pentacyclo[6.2.1.0^{2,7}.0^{4,10}.0^{5,9}]un-decane structure by reduction with NaBH_4 , which is accompanied by transannular cyclisation. When LiAlH_4 is used instead of NaBH_4 , the reaction gives isomeric thiol **10**, in addition to **9**. The compound **9** does not isomerise to **10** under the action of LiAlH_4 ; however, this isomerisation easily occurs upon sublimation of **9** and upon treatment of **9** with methyl iodide in acetone. In the latter case, thiomethylation product **11** is formed together with the thiol **10**. This isomerisation also occurs during the thermolysis of **9** in acetic acid; this gives a mixture of the thiol **10** and bicae sulfides **12a** and **12b** in a ratio of 2 : 1.

The same skeletal transformation accompanies oxidation of the compound **9** with H_2O_2 (1–10 mol) in MeCOOH leading to bicae disulfide **13**, disulfoxide **14** and sulfone **15**. It is noteworthy that each of these compounds is formed as a mixture of two diastereomers **a** and **b** (Scheme 1).¹³

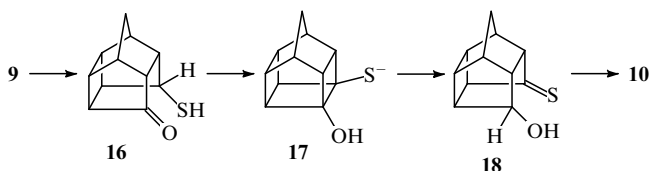
A possible scheme for the above transformation includes the intermediate formation of an open (with respect to the internal thioacetal **9**) form **16**, which is followed by transfer of the chelating proton from sulfur to oxygen, which might lead to

Scheme 1



13: R = SS; **14:** R = SOSO; **15:** R = SO₂.

intermediate **17**. The 'open' hydroxy-thione **18** thus formed is then converted into the corresponding cyclic form, the thiol **10**.

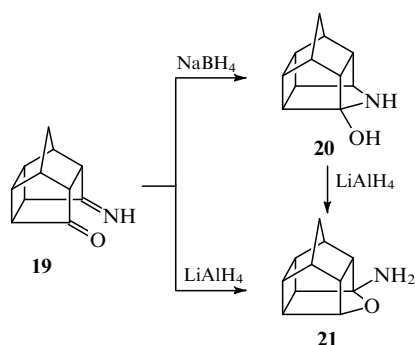


The bicae sulfide **12** results most likely from the interaction of the intermediate **18** with the thiol **10** accompanied by elimination of H_2S . The formation of the compounds **13**–**15** can be rationalised, in turn, in terms of a scheme including isomerisation of **9** to **10** followed by a series of consecutive oxidation stages, **10** → **13** → **14** → **15**. The formation of the latter compound is accompanied by the abstraction of SO_2 .

2. N → O transformations

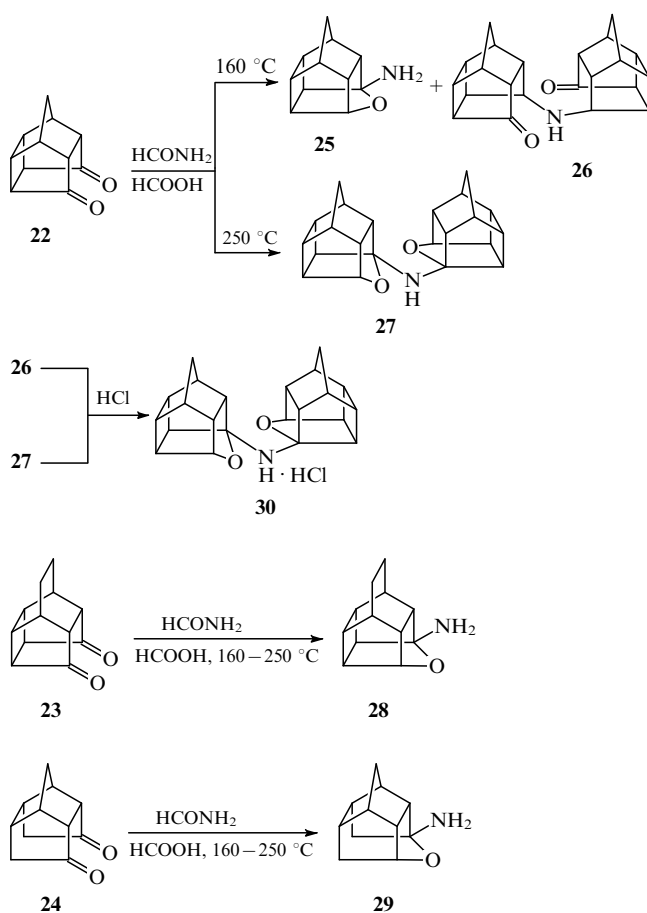
Skeletal transformations with replacement of heteroatoms are also typical of compounds with a bird-cage structure containing a nitrogen atom in the cage. For example, isomerisation of hydroxy-derivative **20** into amino-derivative **21** readily occurs in the presence of LiAlH_4 . When the same reagent is used to reduce imino ketone **19**, the reaction is accompanied by transannular cyclisation and also gives rise to the compound **21**, whereas reduction of the imino ketone **19** with NaBH_4 yields only **20** (Scheme 2).^{14–16} Apparently, a transformation of this sort also occurs during reductive amination of some cage diketones (3,6-diones **22**–**24**) under the action of formamide in formic acid, which is accompanied by transannular cyclisation (Scheme 3).¹⁷ These reactions involve one carbonyl group and afford the corresponding bird-cage primary and secondary amines **25**, **27**–**29** with an oxygen atom in the cage. Secondary amine **26**, which contains fragments of the initial structure and which is formed from the diketone **22** when the reaction is conducted under mild

Scheme 2

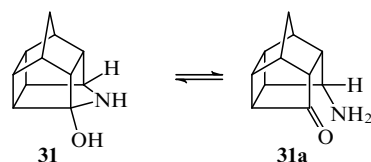
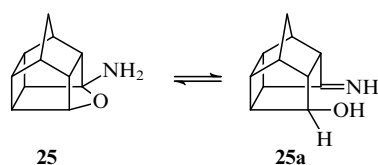


conditions, provides an exception. The fact that the amines **26** and **27** give rise to the same hydrochloride **30** implies that hydrochlorination of the former compound is accompanied by transannular cyclisation and isomerisation.

Scheme 3

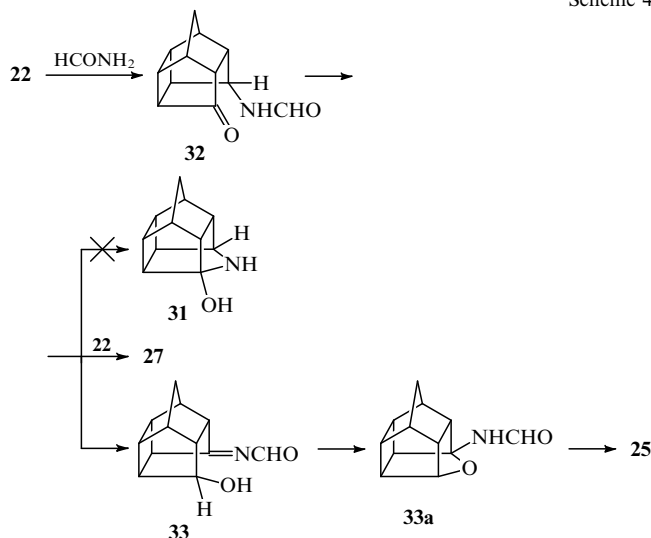


The compounds **25** and **27–29** are internal hemiacetals; the corresponding open derivatives are imino alcohols **25a** rather than amino ketones like **31a**, the formation of which should have been expected in the above reactions.



Using the formation of **25** and **27** as an example, it has been shown that the reductive amination of the 3,6-dione **22** is accompanied by isomerisation; most likely, formamido ketone **32** isomerises to give formimino alcohol **33** (Scheme 4). Apparently, the transformation **32** → **33** occurs similarly to the corresponding isomerisation of sulfur-and-oxygen-containing analogues described above.¹⁷

Scheme 4



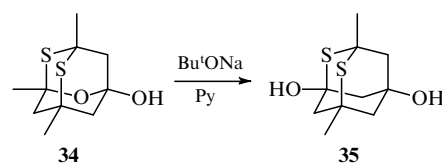
The data presented here indicate that cage compounds with an oxa-bridge are formed preferentially under these conditions. Probably, this is due to the fact that oxygen endows lesser strain to the rigid bird-cage structure than sulfur or nitrogen. Hence, the S → O and N → O type transformations discussed here result in the formation of compounds with a less strained heteroanalogous structure.

III. Skeletal transformations with replacement of oxygen by carbon or of carbon by oxygen

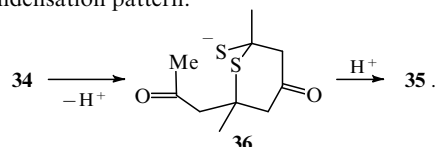
Some transformations of heterocage compounds of the O → C and C → O types have been described; these processes give rise to derivatives with carboanalogous structures containing one oxygen atom more or less in the cage than the initial compound.

1. 'Oxadithiaadamantane → dithiaadamantane' transformation

Treatment of 1-hydroxy-3,5,7-trimethyl-2-oxa-4,6-dithiaadamantane **34** with Bu^tONa in pyridine and then with an acid results in its partial isomerisation to give the dihydroxy-derivative of 3,5-dimethyl-2,4-dithiaadamantane **35**. The proportion of this compound in the mixture of reaction products amounts to 20%–25%.



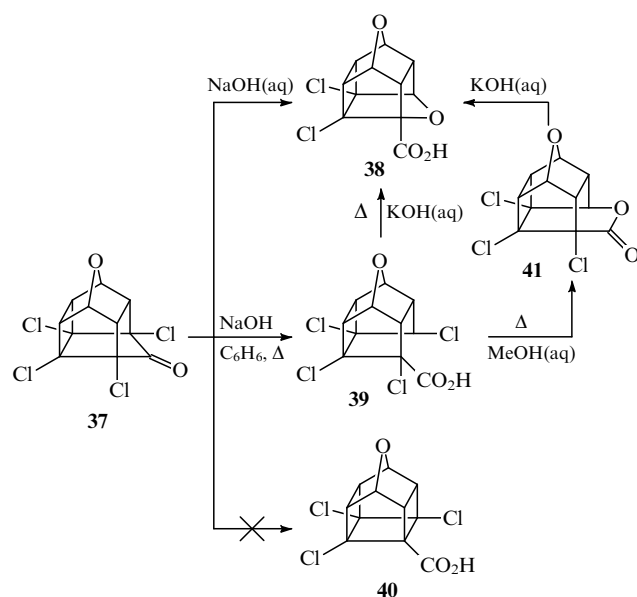
A possible mechanism of this isomerisation includes base-induced ionisation of the compound **34** and subsequent rupture of two bonds; the resulting anion **36** cyclises according to the aldol condensation pattern.¹⁸



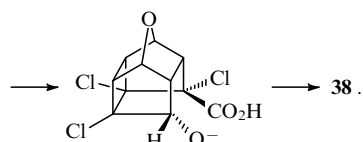
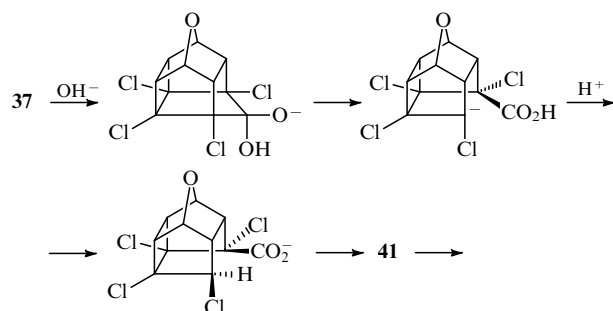
2. C → O transformation

The conversion of the C → O type accompanies the transformation of 1,7,8,11-tetrachloro-ketone **37** having the bird-cage structure and containing one oxygen atom in the cage induced by 25% aqueous NaOH into acid **38** having the bird-cage structure with two oxygen atoms in the cage (yield 66.5%). This acid can be regarded as an abnormal product of the Favorsky rearrangement. If the reaction is carried out in an organic solvent (benzene, THF), it gives rise to another abnormal product, namely, tetrachloro-substituted carboxylic acid **39** with the 11-oxapentacyclo[6.2.1.0^{2,7}.0^{4,10}.0^{5,9}]undecane structure (yield 80.2%). The normal product of the Favorsky rearrangement, acid **40** having a substituted bishomocubane structure, is not formed under the conditions studied. When the acid **39** is refluxed in aqueous KOH, it is converted into the acid **38**, while heating of **39** in aqueous methanol gives rise to lactone **41**. When the latter is kept in aqueous KOH, it is also converted into the compound **38** (Scheme 5).

Scheme 5



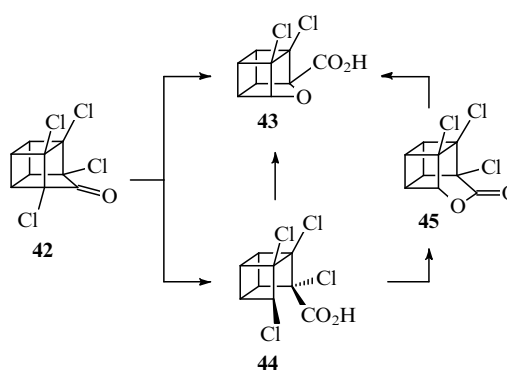
The **37** → **38** transformation occurs most likely by a mechanism that includes formation of the lactone **41**.¹⁹



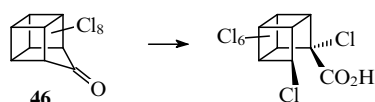
Presumably, the C → O transformation under discussion results in the formation of a less strained structure, because the –O– bridge imparts lesser strain to the rigid bird-cage framework than a carbonyl group incorporated into its 'wing'. At the same time, the resulting structure with two oxygen atoms is certainly less strained than the structure of the bishomocubane oxadervative.

According to the above mechanism, the product **38** is formed without participation of the oxygen bridge already present in the cage. This is confirmed by the occurrence of a similar transformation in the series of carbocage α -halo-ketones. For example, ketone **42** with a homocubane, pentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]-nonanone, structure was converted, depending on the reaction conditions, into chloro-derivative of oxacubanecarboxylic acid **43** or chloro-derivative of secocubanecarboxylic acid **44** (Scheme 6). The **44** → **45** → **43** transformations were also accomplished. In this case, too, no normal Favorsky rearrangement product was obtained.²⁰

Scheme 6

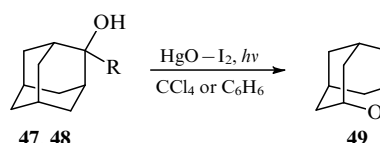


Unlike the tetrachloro-ketone **42**, octachloro-ketone **46** with the same structure is converted under similar conditions only into the octachloro-derivative of secocubanecarboxylic acid.²¹



In many other reactions of cage α -halo-ketones, α -halo-diketones and corresponding ketals, no C → O transformation products have also been obtained.^{21–24} The results presented here make it possible to conclude that the C → O type transformation is peculiar only to those pentacyclic α -halo-ketones in which the structure of the cage and the number and arrangement of halogen atoms ensure additional stabilisation of the corresponding anion.

In addition to the cage (oxa)pentacyclanes discussed above, some 2-substituted adamantanes also undergo this type of transformation. For example, when adamantan-2-ol **47** and its 2-methyl-derivative **48** are exposed to UV radiation in CCl₄ or benzene in the presence of an HgO–I₂ mixture, 2-oxaadamantane **49** is formed in a yield of 43%–47%.^{25,26}



R = H (**47**), Me (**48**).

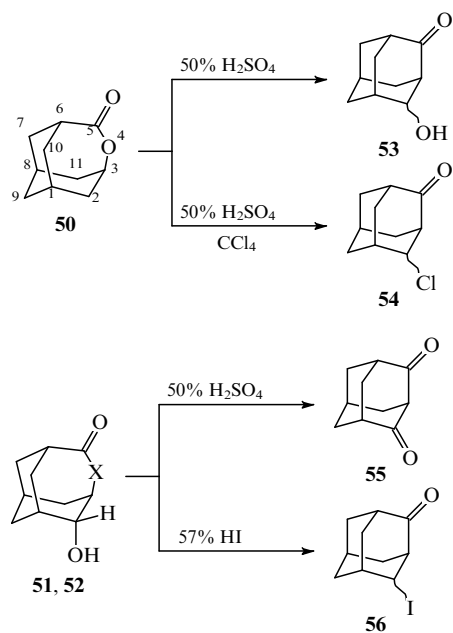
Reactions of these compounds with other oxidants are not accompanied by a skeletal transformation of this type and yield mostly oxahomoadamantane, 4-oxatricyclo[4.3.1.1^{3,8}]undecane, derivatives.^{27–29}

IV. Skeletal transformations of oxacage compounds accompanied by the loss of oxygen and a change in the carbon skeleton

In this Section, we consider reactions of oxacage compounds with electrophiles accompanied by extensive rearrangement of the skeleton. This rearrangement includes opening of the oxygen bridge, loss of the hetero-function and further skeletal transformations resulting in the formation of the corresponding carbocage stabilomer structure.

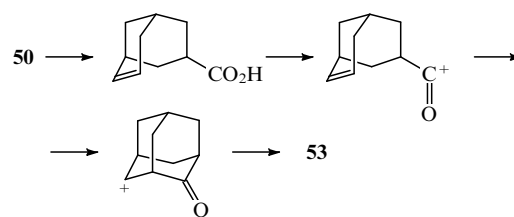
1. Transformations of the ‘oxahomoadamantane → adamantane’ type

On treatment with H₂SO₄ or hydrohalic acids, compounds of the oxahomoadamantane series with oxygen-containing substituents undergo a skeletal transformation yielding functional-substituted adamantane derivatives: C₁₀-tricyclic stabilomers. This transformation is typical of lactone **50**, 2-hydroxy-lactone **51**, 2-hydroxy-lactam **52** and some other compounds. For example, at 90–100 °C in the presence of 50%–80% H₂SO₄, the lactone **50** isomerises into 2-hydroxyadamantan-4-one **53**, which is formed as a mixture of *syn*- and *anti*-isomers in a ratio of 5 : 1.^{30–33} When this reaction is carried out in CCl₄, it gives the product of isomerisation and chlorination, 2-chloroadamantan-4-one **54** (Scheme 7).³⁰ By treatment with 50% H₂SO₄, the hydroxy-derivative **51** has been converted into adamantane-2,4-dione **55** in 22% yield; the reaction of **51** with 57% HI gives 2-iodoadamantan-4-one **56**.³³ The hydroxy lactam **52** reacts with the above reagents to give the same products but in lower yields than the compound **51**; in addition, compounds with non-rearranged structures are formed.³⁴



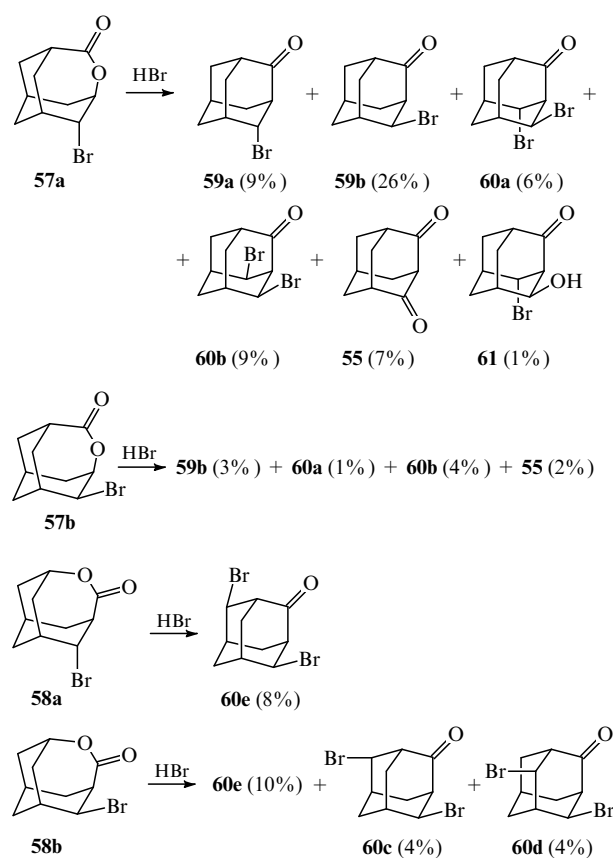
X = O (**51**), NH (**52**).

The mechanism of these transformations presumably includes fragmentation and cyclisation stages.

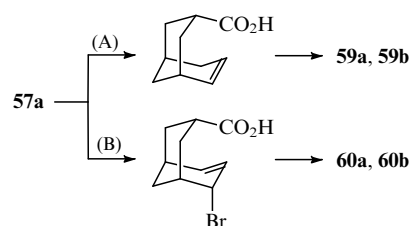


The reactions of individual stereoisomeric 2- and 7-bromo-lactones **57a,b** and **58a,b** with 48% HBr give rise to adamantanone derivatives including stereoisomeric 4-bromides **59a,b**, 4,10-dibromides **60a,b**, 4,8-dibromides **60c,d**, 4a,9e-dibromide **60e**, adamantane-2,4-dione **55** and 4a-hydroxy-10e-bromide **61**. The selectivity of the reaction, the array of reaction products and their proportions in the mixture depend substantially on the positions and spatial arrangement of the substituent in the starting bromo-lactones (Scheme 8).

Scheme 8

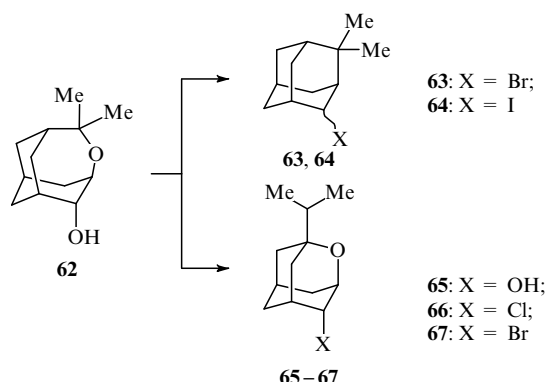


These results are due to the fact that fragmentation can follow either a reductive (type A) or non-reductive (type B) pathway as shown for the bromo-lactone **57**. In this case, pathway A predominates. In the case of the bromo lactones **58a,b**, the fragmentation occurs only by pathway B.³⁵

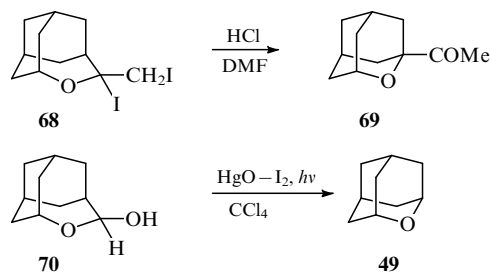


It should be mentioned that the isomeric bromoadamantanones are able to undergo interconversions.³⁶

The transformations under consideration also accompany the reactions of 2-hydroxy-5,5-dimethyl-4-oxahomoadamantane **62** with HBr and HI, which lead to the corresponding 2-halo-4,4-dimethyladamantanes **63** and **64** formed as mixtures of *syn*- and *anti*-isomers.³³

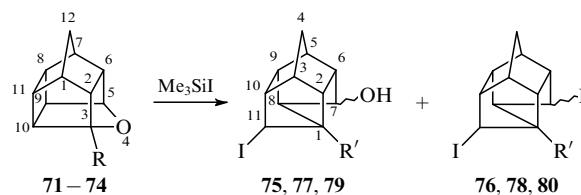


It is noteworthy that the compound **62** undergoes this type of transformation with the loss of oxygen from the cage only under the action of 'hard' reagents. The reactions with 'softer' reagents are accompanied by another skeletal transformation, namely, oxahomoadamantane → oxaadamantane rearrangement. Thus on treatment with 60% H₂SO₄, the compound **62** isomerises into *anti*-4-hydroxy-1-isopropyl-2-oxaadamantane **65**, while the reaction with hydrochloric acid yields a mixture of isomeric chlorides **66** in a ratio of 1 : 1, and the reaction with thionyl bromide gives bromide **67**.³³ This rearrangement also accompanies the reaction of 2-iodo-2-iodomethyloxahomoadamantane **68** with HCl in DMF resulting in the formation of methyl 2-oxaadamantyl ketone **69**^{25–28} and the oxidation of hemiacetal **70** having an oxahomoadamantane structure with the HgO–I₂ system under UV radiation, which gives rise to 2-oxaadamantane.²⁵



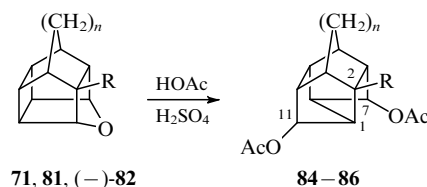
2. 'Bird-cage → trishomocubane' skeletal transformation

Treatment of bird-cage compounds containing an oxygen atom in the cage or their homologues with some electrophilic reagents results in an extensive skeletal rearrangement leading to compounds with the structure of trishomocubane, *i.e.* pentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane. This compound is the stabilomer in the series of cage C₁₁-pentacyclanes.⁹ Compound **71** and its 3-substituted derivatives **72**–**74** were converted into polyiodo- and hydroxyiodo-derivatives of trishomocubane by the reaction with Me₃SiI. The reaction affords one of the above derivatives or their mixture depending on the nature of the substituent and the duration of the process. For example, after 12 h, the compound **71** was converted into 7-hydroxy-11-iodo-derivative **75** in a 48% yield, whereas after 150 h, 7,11-diiodo-derivative **76** was obtained in a yield of 73%.³⁷ The same reaction of methyl-substituted compound **72** gave rise to a mixture of 7-hydroxy-11-iodo-1-methyl-substituted product **77** and 7,11-diiodo-1-methyl-substituted derivative **78**; the compound **73** containing a phenyl group was converted only into 7-hydroxy-11-iodo-1-phenyl derivative **79** under the same conditions. Finally, the 2-hydroxyethyl-substituted compound **74** gave 1-(2-iodoethyl)-7,11-diiodo-derivative **80** in 30% yield.³⁸



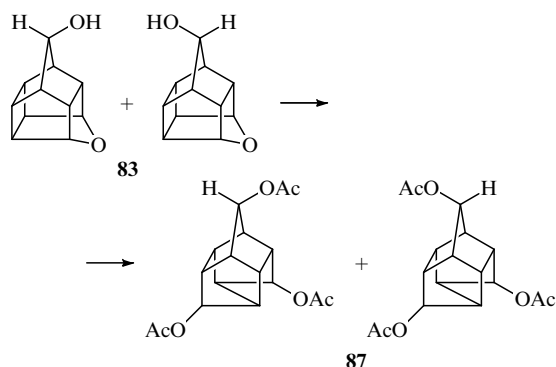
71, **75**, **76**: R = R' = H;
72, **77**, **78**: R = R' = Me;
73, **79**: R = R' = Ph;
74: R = (CH₂)₂OH; **80**: R' = (CH₂)₂I.

The compounds **71**, **81** and **82** undergo a similar skeletal rearrangement under the action of glacial acetic acid in the presence of a catalytic amount of 98% H₂SO₄. In the case of **71**, 7,11-diacetoxytrishomocubane **84** is formed in 15% yield,³⁹ while **81** has been converted into diacetate **85** with the structure of bismethanotwistane, pentacyclo[7.3.0.0^{2,7}.0^{3,11}.0^{6,10}]dodecane, in 24% yield.⁴⁰ The same transformation of the (–)-6-carboxymethyl derivative **82** leads to (–)-2-carboxymethyl-7,11-diacetoxytrishomocubane **86**.^{41, 42}



71, **84**: R = H, *n* = 1;
81, **85**: R = H, *n* = 2;
(–)-**82**, (–)-**86**: R = CH₂CO₂H, *n* = 1.

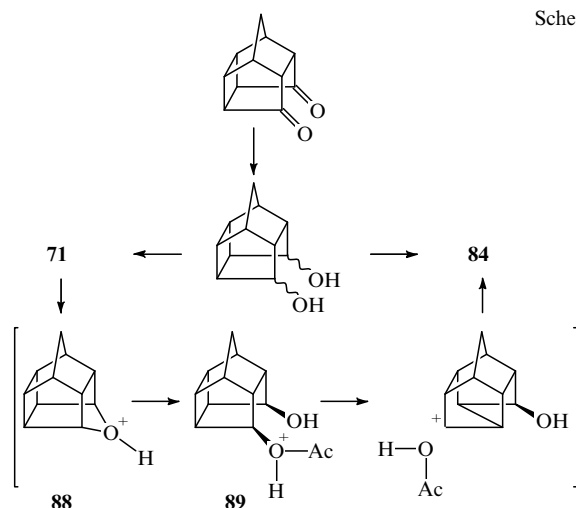
Under similar conditions, a mixture of *syn*- and *anti*-epimers of 12-hydroxy-derivative **83** has been converted into a mixture of epimeric 7,11,12-triacetoxytrishomocubanes **87**.⁴³



The mechanism of this rearrangement, which has been discussed in relation to **71**, includes the formation of the protonated ether **88**, which undergoes a nucleophilic attack by MeCOOH to give intermediate **89**. The latter undergoes a skeletal rearrangement with opening of the four-membered ring, similar to the corresponding rearrangement in the series of the carbo-analogue, which results in the formation of the trishomocubane structure (Scheme 9).³⁹

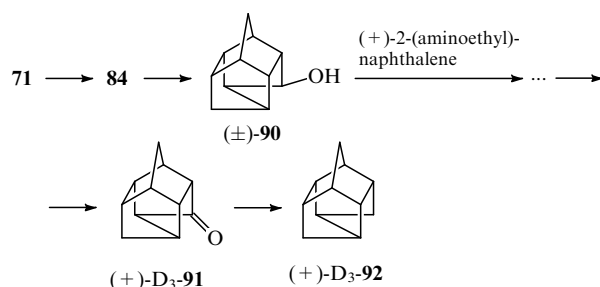
Compounds with the bird-cage structure containing an oxygen atom in the cage and related compounds are formed from derivatives of pentacyclo[6.2.1.0^{2,7}.0^{4,10}.0^{5,9}]undecane and its homologues, as has been shown for the compound **71**. Thermodynamically controlled isomerisation of bird-cage derivatives makes it possible to prepare di- and tri-substituted trishomocubanes the syntheses of which are described in this Section.^{44–50} Of the two alternative routes mentioned above, it is the synthesis based on bird-cage compounds with an oxygen atom in the cage

Scheme 9

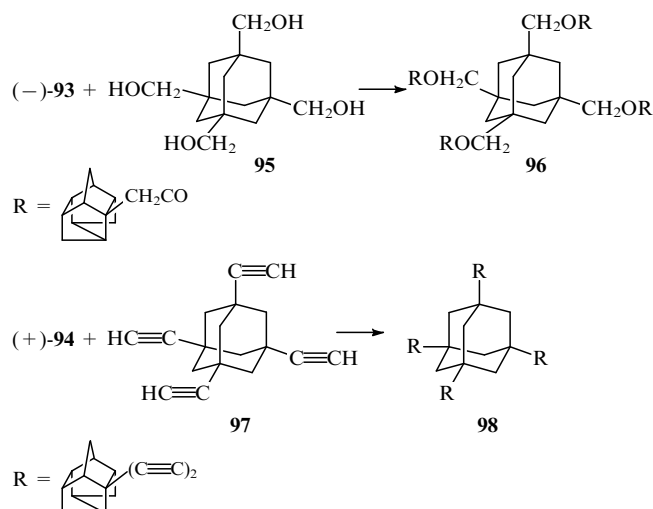
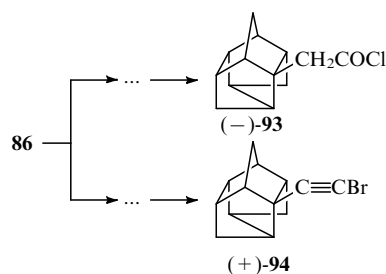


(the so-called modified Barborac method) that proved to be more convenient from the preparative viewpoint, because none of its steps yields side products or mixtures of isomers. Therefore, this method has found application in the preparation of key synthons for the syntheses of optically active organic molecules with *T*-symmetry and a known absolute configuration.

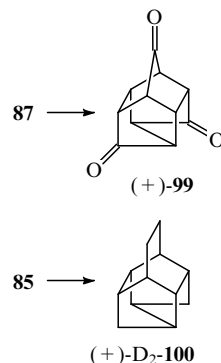
For example, by a series of transformations of bird-cage compounds, including preparation of ($\pm$)-hydroxytrishomocubane **90**, the synthesis of (+)-D₃-trishomocubane **91** and (+)-D₃-trishomocubane **92** has been accomplished.^{51, 52}



The compound **86** obtained by this skeletal rearrangement has served as a key intermediate in the synthesis of 2-substituted trishomocubane derivatives, namely, acid chloride (–)-**93** and ethynyl bromide (+)-**94**. The reaction of the former with 1,3,5,7-tetrakis(hydroxymethyl)adamantane **95** has given rise to compound (–)-**96**,⁴² whereas the latter reacts with 1,3,5,7-tetra(ethynyl)adamantane **97** to give compound (+)-**98**.^{53, 54}



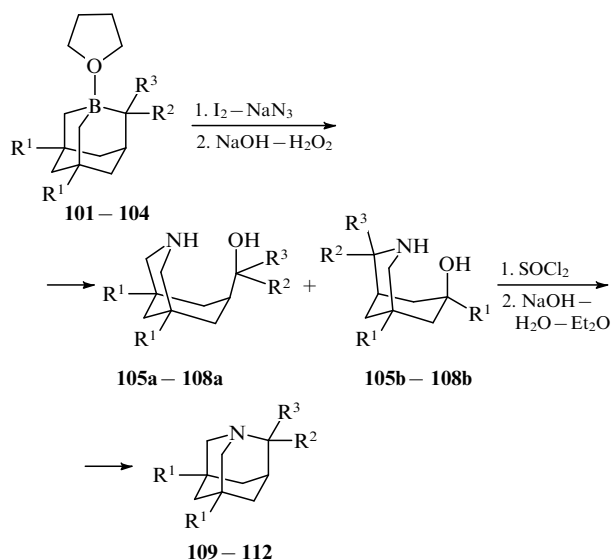
Optically active (+)-triketone **99** with the trishomocubane structure was synthesised from a mixture of epimeric 7,11,12-triacetates **87**,⁵¹ while the diacetate **85** was converted into (+)-D₂-bismethanotwistane **100**.⁴⁰



V. Syntheses based on boraadamantanes accompanied by rearrangements involving the boron atom

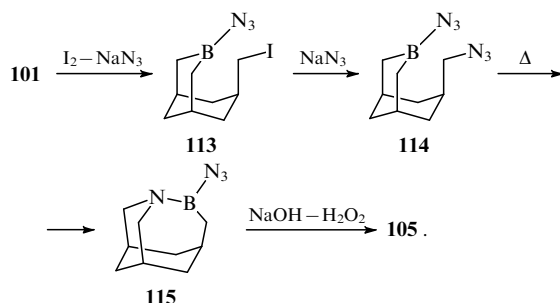
Cage derivatives of boron can be used as key intermediates in the syntheses of compounds of the adamantane series including aza- and oxa-derivatives.^{55, 56} The transition from bora-containing compounds to other structures is accomplished *via* skeletal rearrangements. Various types of transformations are known, including those in which the boron atom is replaced by a nitrogen or carbon atom or in which the bridging boron atom is displaced from the cage.

The skeletal rearrangement of the B → N type is the key stage in the transformation of compounds **101**–**104** of the 1-boraadamantane series into 1-azaadamantane **109** and its alkyl derivatives **110**–**112**, which are difficult to prepare by any other method. For example, iodination of the tetrahydrofuran complexes **101**–**104** in the presence of NaN₃ followed by oxidation of intermediate compounds by the NaOH–H₂O₂ system gives rise to mixtures of isomeric amino alcohols **105**–**108** with the 3-azabicyclo[3.3.1]nonane structure; cyclisation of these products in the presence of SOCl₂ affords the corresponding compounds **109**–**112** in an overall yield of 15%–40%.^{57–59}

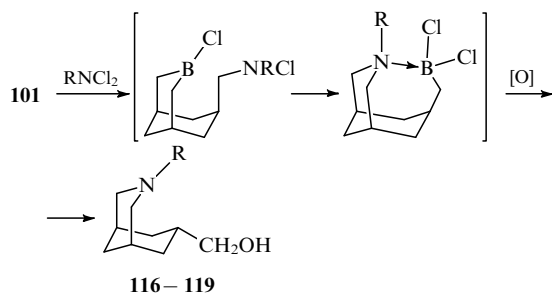


101, 105, 109: $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{H}$;
102, 106, 110: $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{R}^3 = \text{H}$;
103, 107, 111: $\text{R}^1 = \text{R}^2 = \text{H}$, $\text{R}^3 = \text{Me}$;
104, 108, 112: $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{R}^3 = \text{Me}$.

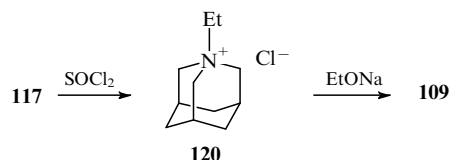
A possible mechanism for this reaction accompanied by a skeletal rearrangement, which is considered in relation to the compound **101**, includes fragmentation with cleavage of one of the B–C bonds and formation of 3-azido-7-iodomethyl-3-borabicyclo[3.3.1]nonane **113**. The latter reacts with excess NaN_3 to give diazide **114**, which undergoes thermal 1,2-anionotropic rearrangement and subsequent cyclisation to give 2-azido-1-aza-2-borahomoadamantane **115**. This is followed by fragmentation accompanied by the loss of boron and yielding the compound **105**.



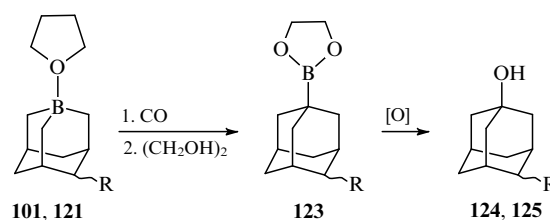
The B $\rightarrow$ N transformation has also been observed in the amination of 1-boraadamantane with alkylchloroamines. *N*-Alkyl-derivatives of 3-azabicyclo[3.3.1]nonane (**116–119**) were obtained in this way. On treatment with SOCl_2 , the *N*-ethyl-substituted compound **117** cyclises to give quaternary salt **120**; its subsequent fragmentation leads to the 1-azaadamantane **109**.^{60, 61}



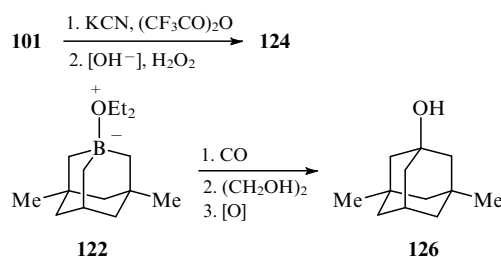
$\text{R} = \text{Me}$ (**116**), Et (**117**), Pr (**118**), Bu (**119**).



Carbonylation of 1-boraadamantane derivatives **101, 121** and **122** in the presence of ethylene glycol is accompanied by skeletal transformation in which the boron atom is replaced by a carbon atom. The oxidation of the resulting ethylene glycol ester of 1-adamantylboronic acid **123** (or the corresponding derivatives) affords compounds of the adamantane series. Thus the compound **101** was converted into adamantan-1-ol **124** in 78% yield, the 4-chloro-derivative **121** gave the 4-chloro-1-hydroxy-derivative **125** (in a low yield) and the reaction of etherate **122** resulted in the formation of 1-hydroxy-3,5-dimethyladamantane **126** (yield 95%).^{62, 63} It should be noted that the **101** $\rightarrow$ **124** transformation can also be accomplished using the $\text{KCN} - (\text{CF}_3\text{CO})_2\text{O}$ system.⁶²

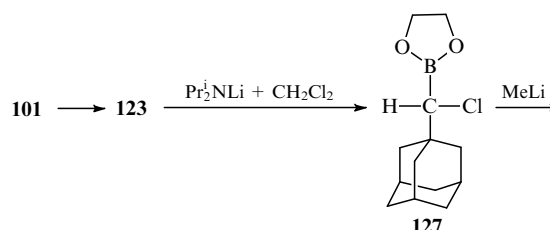


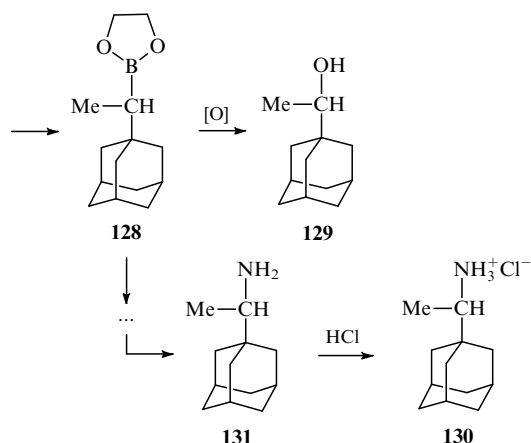
$\text{R} = \text{H}$ (**101, 124**), Cl (**121, 125**).



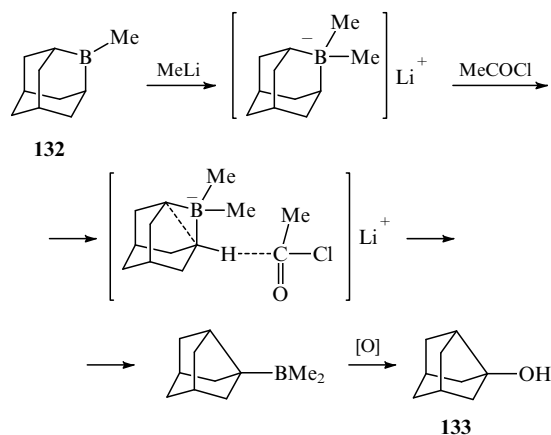
Treatment of the carbonylation products **123** with dichloromethylithium affords chloride **127**. When this product is treated, without isolation, with methylithium, it is converted into compound **128**, oxidation of which yields 1-(1-hydroxyethyl)adamantane **129**.⁶⁴

Based on this skeletal transformation of 1-boraadamantane **101**, a new method for the synthesis of remantadine **130**, a known antiviral drug, has been developed. 1-(1-Aminoethyl)adamantane **131** was obtained in a yield of 38% with respect to the initial boraadamantane **101**. The salt **130** was prepared by treating the free base **131** with HCl in ether.⁶⁴





Complexes of cage boratrimethylsilyl compounds with lithiumalkyls are capable of reducing (by hydride transfer) some types of organic compounds; this reaction is accompanied by rearrangement of the boratrimethylsilyl cage. This rearrangement in which the boron atom is removed from the cage makes it possible to proceed from 2-methyl-2-boraadamantane **132** to 1-hydroxynoradamantane **133**.⁶⁵



VI. Conclusion

It follows from the reactions considered above that skeletal transformations typical of functionally substituted cage heterotricyclanes and heterohexacyclanes are quite diverse and can be induced by various reagents under mild conditions. The reactions of functionally substituted thia- or aza-cage compounds accompanied by cage rearrangements and by replacement of the sulfur or nitrogen atom by oxygen give rise to compounds with the oxacage skeleton, which is less strained than the initial structures. Oxacage derivatives, in turn, can be converted under certain conditions into the corresponding stabilomer carbocage structures.

Thus, the information presented in this review not only considerably supplements the general scheme of known skeletal modifications of cage compounds, but also markedly extends the views about the synthetic potential of the rearrangements of hetero(poly)cyclanes leading to the replacement, introduction or removal of the hetero-function.

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Selenium-containing heterocycles

V P Litvinov, V D Dyachenko

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Abstract. The literature data, mainly of the last ten years, on the synthesis, reactions, and practical utilisation of selenium-containing heterocycles are analysed, treated systematically, and surveyed. The bibliography includes 516 references.

I. Introduction

Organoselenium compounds have continued to attract the attention of a wide range of investigators owing to a series of their unique properties. At the Second International Symposium on the Chemistry and Biochemistry of Organic Compounds of Selenium and Tellurium, it was noted that the deficiency of selenium in the human and animal organisms constitutes the basis of various chronic diseases, in particular the necrosis of the liver.^{1,2} There are data showing that organoselenium compounds are capable of sensitising processes in the living organism,³ which includes the inhibition of anomalous oxidation processes with the aid of the Se^{2–} containing glutathioneperoxidase active group.¹ Four proteins containing a selenium atom are known among natural products.⁴ Therefore, despite the high toxicity of many selenium compounds,^{5–7} antitumour,^{8–10} anticancer,^{11,12} and other medicinal preparations,^{13–21} as well as biologically active substances exhibiting antiviral,^{22–26} antimicrobial,^{27–30} antiarrhythmic,³¹ and fungicidal^{32–36} activities have been produced on the basis of organic derivatives of selenium. Furthermore, superconducting materials³⁷ as well as dyes,^{38–48} including those suitable for electrophotography,^{49–53} have been prepared on their basis.

Heterocycles containing a selenium atom occupy a special place among organoselenium compounds. Although numerous reviews on various aspects of the chemistry of organoselenium compounds have been published during the last ten years,^{54–74} the survey of literature data on organoselenium heterocycles is restricted to pre-1985.^{74–77} It therefore appears useful to analyse

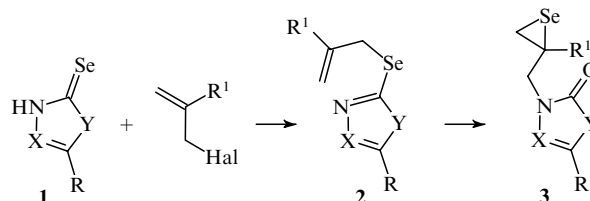
the data on selenium-containing heterocycles, concentrating attention on studies of recent years.

The size of the heterocycle and not the method of synthesis has been selected as the criterion for the systematic arrangement of data on selenium-containing heterocycles. To achieve a more compact exposition and to eliminate the possibility of duplicating data, the chemical and other properties of the compounds considered are quoted together with the methods of their synthesis.

II. Three-membered heterocycles

1. Seleniranes

Until recently, seleniranes (episelenides) had not been obtained in a pure form, in contrast to their sulfur analogues (thiiranes),⁷⁸ although their formation in the flash photolysis of CSe₂ had been reported,^{79–81} which was confirmed in a mass-spectrometric study.⁸² Later the formation of seleniranes as intermediates was postulated in reactions involving the specific conversion of oxiranes,^{83–86} the cyclisation of *para*-substituted allyl phenyl selenides,⁸⁷ the conversion of bromohydrins into alkenes on treatment with potassium selenocyanate⁸⁸ or of 1,2-dibromethane into ethene in the presence of the selenodithiocarbonate anion,⁸⁹ and in the desulfurisation of thiiranes with 3-methyl-2-selenoxobenzothiazole.⁹⁰ The decomposition of the intermediate seleniranes with liberation of selenium was noted in all the examples quoted above. It was not until the end of the 1990s that reports of the synthesis of substituted seleniranes by the alkylation of heterocyclic selenones **1** and the subsequent transformation of the selenides **2** into substituted seleniranes **3**^{91,92} or by the interaction of the azoles **4** with selenium and epichlorohydrin with formation of the seleniranes **5**⁹³ appeared although without the specification of experimental data.

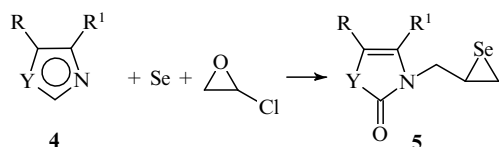


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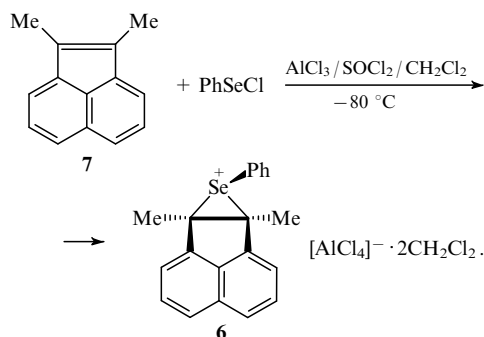
Uspekhi Khimii 66 (11) 1025–1053 (1997); translated by A K Grzybowski



R = Alk, Ar; R¹ = H, Me; X = CR, N; Y = NR, S; Hal = Br, I.

2. Seleniranium salts

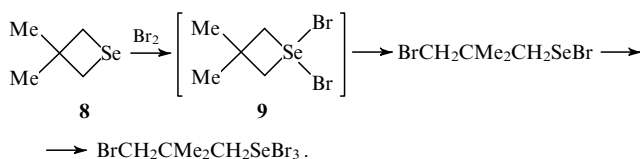
The formation of seleniranium (episelenonium) salts as intermediates has been noted in a series of studies,^{94–104} but it was not until 1986 that data concerning the synthesis of the stable episelenonium salt **6** as a result of the treatment of 1,2-dimethyl-acenaphthylene **7** with PhSeCl in the AlCl₃–SOCl₂–CH₂Cl₂ system at –80 °C were published.¹⁰⁵ According to X-ray (XRD) data, a characteristic feature of the structure of the episelenonium ring in the salt **6** is the appreciable lengthening of the Se⁺–C bond compared with the corresponding bonds in trimethylselenonium,¹⁰⁶ which causes their lower stability. It has also been shown that the benzene and acenaphthene rings in the salt **6** are in the *cis*-position not only in the solid state but also in solution.



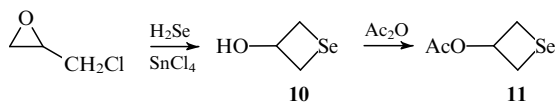
III. Four-membered heterocycles

1. Selenetanes

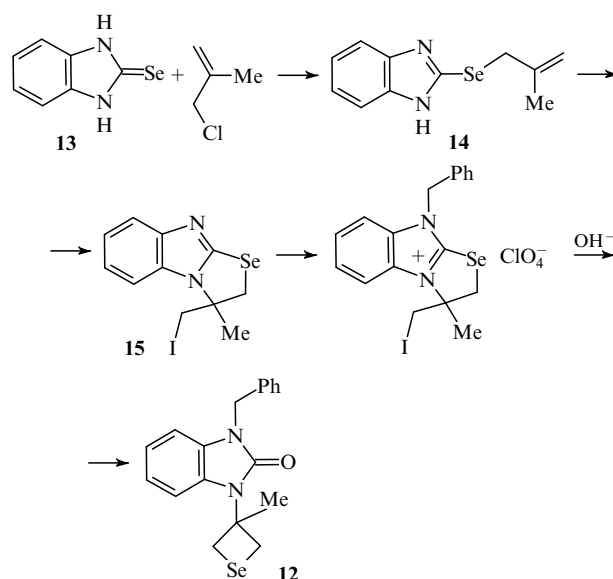
Unsubstituted selenetane was first obtained in a low yield in 1930¹⁰⁷ by treating 1,3-dibromopropane with alkali metal selenides. Selenetane readily polymerises and can be stored only at reduced temperatures in the dark. 3,3-Dimethylselenetane **8** is more stable (up to 140 °C),^{108, 109} whereas its dibromo-derivative **9** is stable only at temperatures below –20 °C; when the temperature is raised, the selenetane ring is opened.^{108, 110}



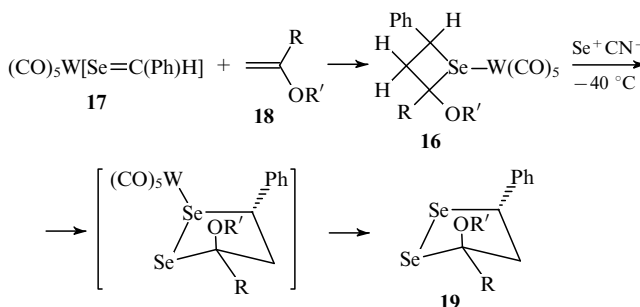
Selenetan-3-ol **10** is a stable compound. It is formed in 58% yield as a result of the reaction of epichlorohydrin with hydrogen selenide at 60 °C in the presence of tin chloride or toluene-*p*-sulfonic acid¹¹¹ or on decomposition of the salt Hg(II) 1,3-diselenylpropan-2-olate.¹¹² Treatment of the selenetan-3-ol **10** with acetic anhydride leads to the acetate **11**.¹¹⁰



The substituted selenetane **12** is obtained by means of a scheme involving in the first stage the alkylation of the heterocyclic selenone **13** with formation of the selenide **14**, which affords benzimidazo[2,1-*a*]selenazolidine **15** on iodocyclisation. As a result of a series of reactions, involving quaternisation and recyclisation, compound **15** gives rise to the selenetane **12**.¹¹³



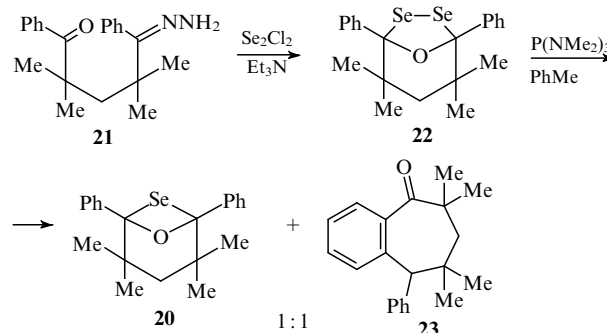
The pentacarbonyltungsten complexes of the selenetane **16** are formed when complex **17** is treated with an excess of vinyl ethers.^{114, 115} Complex **16** reacts with an excess of selenocyanate already at –40 °C in the course of several minutes with formation of the diselenolanes **19**. The structure of one of them (R = R' = Me) has been confirmed by XRD data.¹¹⁵



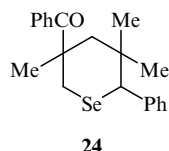
R = H, R' = Et; R = R' = Me.

2. Oxaselenetanes

Four-membered heterocycles containing one oxygen atom and one selenium atom (oxaselenetanes) are known intermediates in the oxidation reactions of exocyclic alkenes by means of SeO₂/H₂O₂.¹¹⁶ The bicyclic 1,3-oxaselenetane derivative **20** was obtained by refluxing 2,2,4,4-tetramethyl-1,5-diphenylpentane-1,5-dione monohydrazone **21** with Se₂Cl₂ in the presence of triethylamine.^{117–119} The reaction proceeds *via* a stage involving the formation of the 1,3,4-oxadiselenolane **22**, the treatment of which with P(NMe₂)₃ or PPh₃ leads to a 1 : 1 mixture of oxaselenetane and benzosuberone derivatives **20** and **23** respectively.

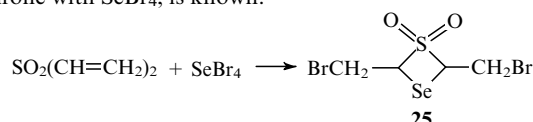


After refluxing the reaction mixture for 10 h, the substituted selenacyclohexane **24** is also formed.¹¹⁹



3. Thiaselenetanes

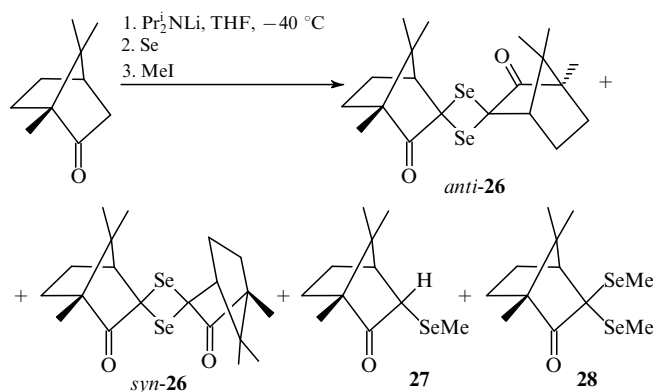
Among four-membered heterocycles containing sulfur and selenium atoms, the thiaselenetane **25**, formed on treating divinyl sulfone with SeBr_4 , is known.¹²⁰



4. Diselenetanes

Many examples of four-membered heterocycles with two selenium atoms are known. Thus 3,4-bis(trifluoromethyl)-1,2-diselenetane has been obtained in 25% yield on pyrolysis of a mixture of bis(trifluoromethyl)ethyne and selenium.^{121,122} 1,3-Diselenetanes are synthesised by various methods: the pyrolysis of 1,2,3-selenadiazole¹²³ and the reactions of dimethyl malonate with CSe_2 ,¹²⁴ of acetylacetone with SeCl_4 ,¹²⁵ of acetyl chloride with H_2Se and AlCl_3 ,¹²⁶ and of hexafluoroacetone with triphenylphosphine selenoxide.¹²⁷

It has been observed recently that the reaction of the lithium enolate of camphor with selenium and subsequent treatment of the reaction mixture with methyl iodide lead to a mixture of the *syn*-(32%) and *anti*-(10%) isomers of 1,3-diselenetane **26** together with methyl selenide **27** (12%) and the diselenoacetal **28** (15%).¹²⁸ The structure of the *anti*-isomer **26** was confirmed by XRD.



IV. Five-membered heterocycles

The vast majority of studies on the chemistry of selenium-containing heterocycles have been devoted to five-membered heterocycles owing to their relative resistance to the action of various kinds of reagents (by virtue of their aromaticity, the small Bayer strain, and the absence of Pitzer strain) as well as their great practical importance.

Compounds with the properties of semiconductors,^{129,130} polymethine dyes,^{131–134} photosensitisers,^{135–144} as well as substances exhibiting various types of biological activity (antimicrobial,¹⁴⁵ antiviral,¹⁴⁶ antitumour,^{147–150} glutathioneperoxidase,¹⁵¹ spasmolytic,^{152,153} antiallergic,¹⁵⁴ antiherpetic,¹⁵⁵ and fungicidal^{156–158}) are known among derivatives of this class.

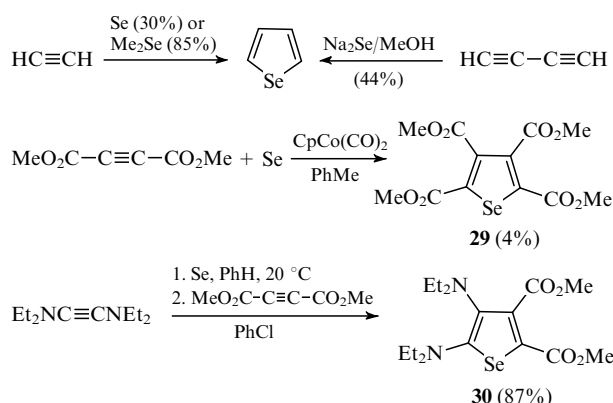
1. Five-membered heterocycles with one heteroatom

a. Selenophenes

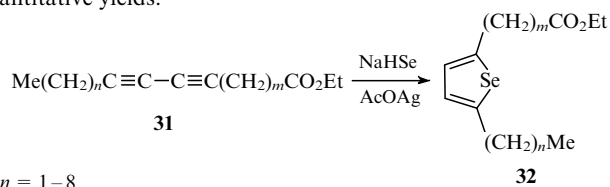
Selenophene and its derivatives have been most thoroughly investigated among five-membered selenium-containing heterocycles. The continued interest in selenophene has been reflected periodically in published reviews.^{159–162}

Fairly numerous new methods of synthesis of selenophene and its derivatives have been developed during the last decade. One of them involves the interaction of acetylene and its derivatives with elemental selenium. Selenophene has been obtained in this way in 30% yield¹⁶³ together with its derivatives **29** (4%)¹⁶⁴ and **30** (87%).¹⁶⁵

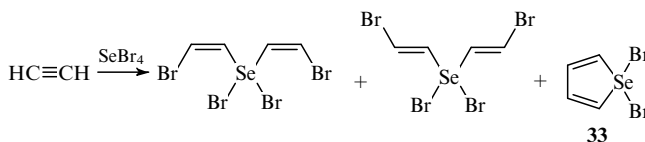
Selenophene may be obtained in 85% yield by the reaction of acetylene with dimethyl selenide in the gas phase¹⁶⁶ and also by treating diacetylene with sodium selenide in methanol (yield 44%).¹⁶⁷ In addition, it has been shown that 2% of selenophene is also obtained on heating dimethyl selenide in a quartz tube at 470 °C.¹⁶⁸



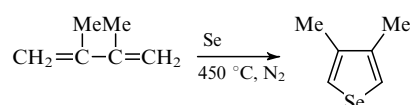
The interaction of sodium hydroselenide with diethynes **31** results in the formation of 2,5-disubstituted selenophenes **32** in quantitative yields.¹⁶⁹



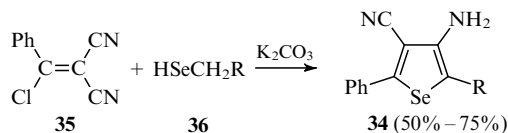
On interaction with selenium tetrabromide, unsubstituted acetylene affords a mixture of bromine-substituted selenides, including selenophene dibromide **33**.¹⁷⁰



Other unsaturated compounds have also found application in the synthesis of selenophenes. Thus buta-1,3-diene reacts with selenium dioxide in the presence of Zeokar 2 as the catalyst with formation of selenophene in 45% yield.¹⁷¹ 3,4-Dimethylselenophene is formed in up to 80% yield from 2,3-dimethylbuta-1,3-diene on interaction with powdered selenium in the presence of sand or glass fragments at 450 °C under a nitrogen atmosphere.¹⁷²

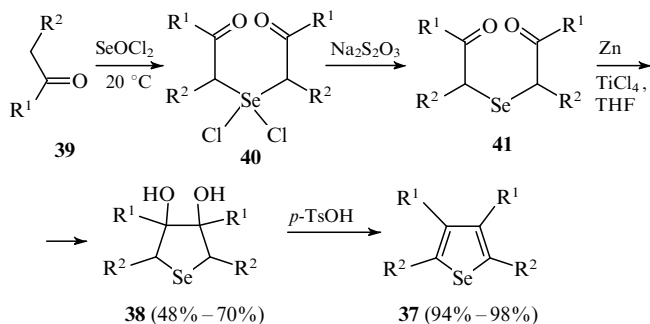


The synthesis of functionally substituted selenophenes **34** on interaction of the nitrile **35** with alkaneselenols **36** has also been reported.¹⁷³



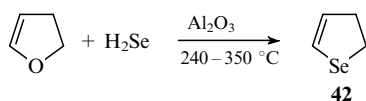
R = Ac, PhCO, CN, NO₂, CHO, COOH, CO₂Et.

The method of synthesis of substituted selenophenes **37** by the dehydration of selenolanediols **38** has been described.¹⁷⁴ The diols were obtained in accordance with the following scheme: the interaction of selenium oxychloride with the ketones **39** to form the chlorinated selenides **40** which are readily reduced by sodium thiosulfate in benzene to the selenide **41**, and subsequent treatment with TiCl₄ and Zn in tetrahydrofuran (THF) at 0 °C.

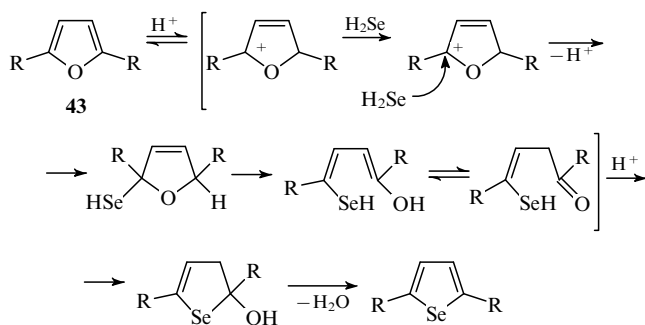


R¹ = Ar, Het; R² = H, Me.

The transformation of furan and thiophene into selenophene on treatment with hydrogen selenide or elemental selenium, used for the synthesis of 2,3-dihydroselenophene **42**, is well known.¹⁷⁵

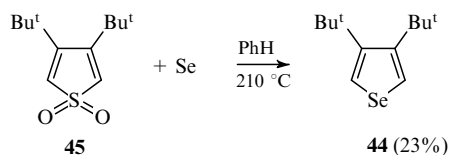


The mechanism of this reaction has been investigated relatively recently. It has been established in relation to the interaction of the furans **43** with hydrogen selenide that the reaction proceeds *via* a mechanism involving specific acid catalysis including a stage with a doubly protonated substrate.^{176, 177}



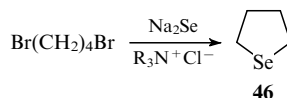
R = H, Me.

3,4-Di(*tert*-butyl)selenophene **44** has been obtained in 21% yield by treating 3,4-di(*tert*-butyl)thiophene 1,1-dioxide **45** with powdered selenium in benzene in an autoclave at 210 °C.¹⁷⁸

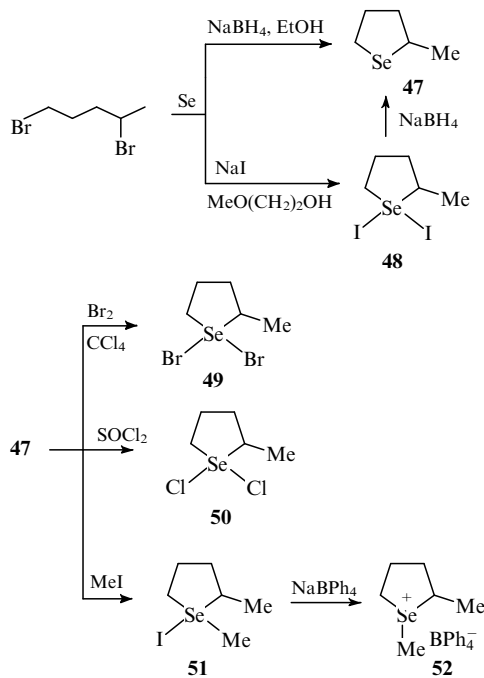


b. Selenolanes

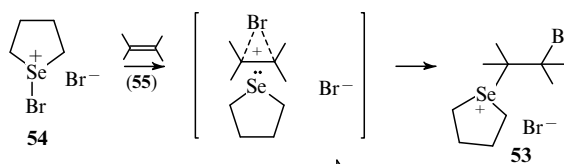
A simple method of synthesis of selenolane **46**, by refluxing 1,4-dibromobutane with sodium selenide under a nitrogen atmosphere under the conditions of phase-transfer catalysis, has been developed. Alkyl(C₈–C₁₀)ammonium chlorides were used as the catalysts.¹⁷⁹



2-Methylselenolane **47** has been obtained¹⁸⁰ in two ways. The refluxing of 1,4-dibromopentane with a 1 : 1 mixture of Se and NaI in solution in the monomethyl ether of ethylene glycol leads to the diiodide **48** in 27% yield, which is reduced with NaBH₄ to 2-methylselenolane. The reaction of 1,4-dibromopentane with elemental selenium in alcohol in the presence of sodium tetrahydroborate under an argon atmosphere leads to compound **47** in 78% yield. Certain reactions of 2-methylselenolane have been investigated. Thus, on interaction with bromine in CCl₄, it gives rise to the dibromide **49**, while its interaction with SOCl₂ affords the dichloride **50** in 85% yield. Treatment of 2-methylselenolane **47** with MeI leads to compound **51** which on reaction with NaBPh₄ is transformed into the salt **52**.

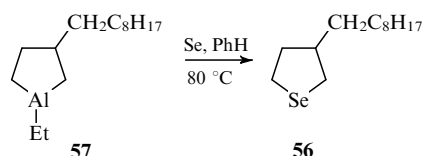


The interaction of tetramethyleneselenonium bromide,⁵⁴ obtained from selenolane and bromine, with the alkenes **55** in acetonitrile at 20 °C leads to the β-bromoselenonium salts **53** in yields ranging from 50% to 75%.¹⁸¹ The reaction proceeds in accordance with the Markovnikov rule as stereospecific electrophilic addition with formation of *trans*-adducts.

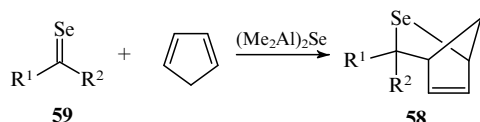


55: C₅H₁₁CH=CH₂, , , .

The interaction of 3-nonylaluminacyclopentane **57** with elemental selenium on refluxing in benzene has been used in the synthesis of 3-nonylselenolane **56**.¹⁸²

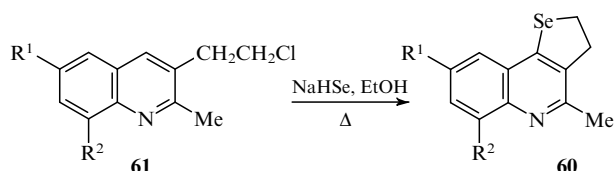


A method based on the interaction of selenocarbonyl compounds **59** with cyclopentadiene has been proposed for the synthesis of bicyclic selenolane derivatives — selenabicycloheptenes **58**.^{183–187}



$\text{R}^1, \text{R}^2 = \text{H, Me, Ph, SiMe}_3$; $\text{R}^1 - \text{R}^2 = (\text{CH}_2)_5$.

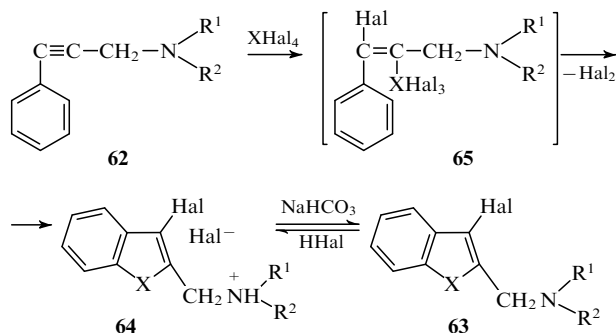
The interaction of 2-chloroethyl derivatives of the quinolines **61** with sodium hydroselenide in ethanol has been used in the synthesis of condensed derivatives of the selenolanes **60** containing a quinoline fragment; the yield of the selenolanes **60** then reaches 45%–58%.¹⁸⁸



$\text{R}^1, \text{R}^2 = \text{H, Me, OMe, Cl}$.

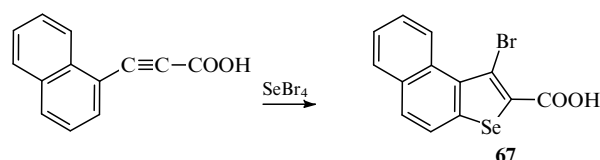
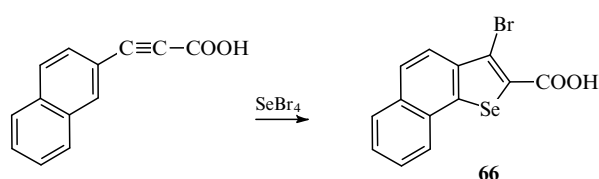
c. Condensed selenophenes

Substituted acetylenes, which give rise to both benzo- and naphtho-selenophenes on interaction with selenium tetrahalides, have been used successfully in the synthesis of condensed selenophenes. Thus a preparative method of synthesis of aminomethyl derivatives of benzo[*b*]thio(seleno, telluro)phenes **63** and their hydrohalides **64** has been developed on the basis of the interaction of chalcogen halides with 3-phenylpropynylamines **62**.¹⁸⁹ The reaction proceeds with formation of the intermediates **65**.

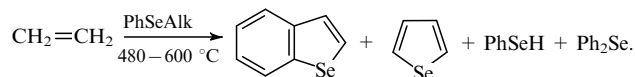


$\text{R}^1 = \text{H, Me, Et}$; $\text{R}^2 = \text{Me, Et}$; $\text{R}^1, \text{R}^2 = (\text{CH}_2)_5, (\text{CH}_2)_2\text{O}(\text{CH}_2)_2$;
 $\text{X} = \text{S, Se, Te}$; $\text{Hal} = \text{Br, Cl}$.

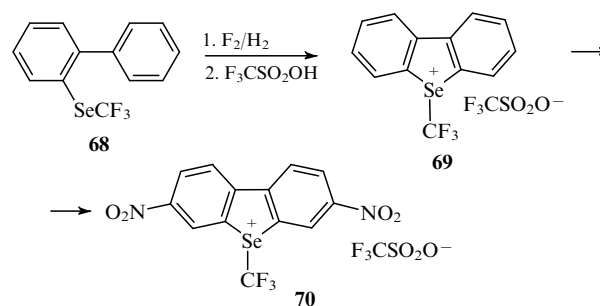
The similar treatment of 3-(2-naphthyl) and 3-(1-naphthyl)-propionic acid derivatives with selenium tetrabromide leads to the substituted naphthoselenophenes **66** and **67**.¹⁹⁰



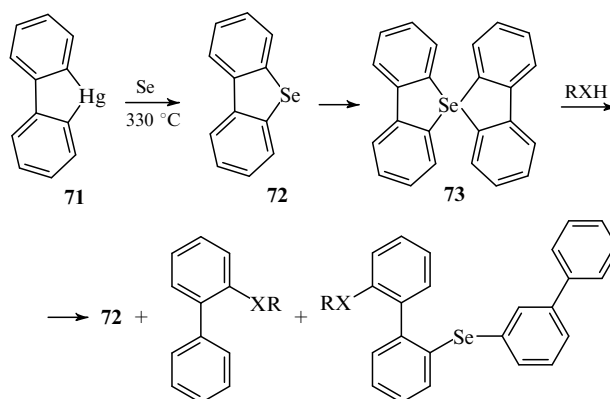
Ethene reacts with alkyl phenyl selenides at high temperatures ($480\text{--}600^\circ\text{C}$) to form benzoselenophene (yield 25%), selenophene, and other organo-selenium compounds.¹⁹¹



2-Biphenyl trifluoromethyl selenide **68** has been used to obtain the dibenzoselenophene salt **69**, which is readily converted into the corresponding dinitro-derivative **70**.¹⁹²

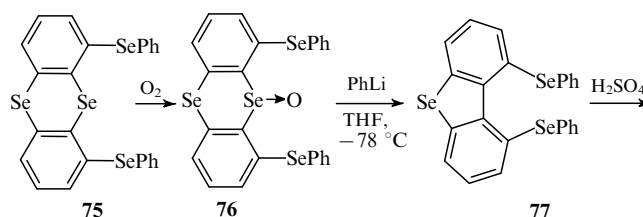


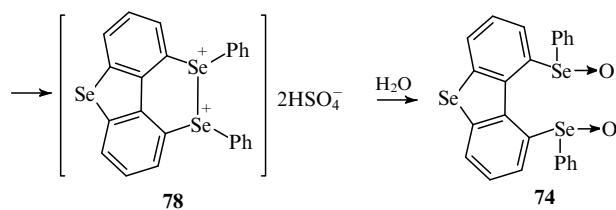
On heating with elemental selenium, 9-mercurofluorene **71** affords dibenzoselenophene **72**, which readily dimerises to the selenurane **73**¹⁹³ and the latter reacts with alcohols, thiols, and selenols in THF at -78°C under an argon atmosphere to form a mixture of products, one of which is dibenzoselenophene **72**.¹⁹⁴



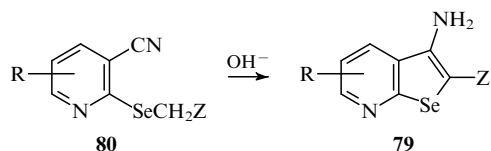
$\text{R} = \text{Me, Et, Pr, Pr}^i, \text{Ph}$;
 $\text{X} = \text{O, S, Se}$.

A method of synthesis of the disubstituted dibenzoselenophene **74** via a scheme involving the oxidation of selenanthrene **75** and the reduction of the resulting selenoxide **76** to compound **77** has also been described. Treatment of the latter compound with sulfuric acid leads to the dioxide **74**. It has been established by NMR that the reaction proceeds via the dication **78**.¹⁹⁵





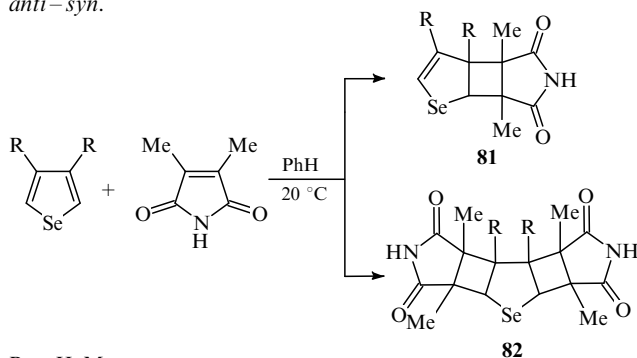
The Thorpe–Ziegler cyclisation of pyridine-series selenides **80** has been used successfully in recent years for the synthesis of functionally substituted selenopheno[2,3-*b*]pyridines **79**.^{69, 196–221}



R = H, Ar, Het, Alk, NH₂, CO₂Alk, OH, CN;
Z = CN, CO₂Alk, COAr, COHet, CONHAr, CONH₂.

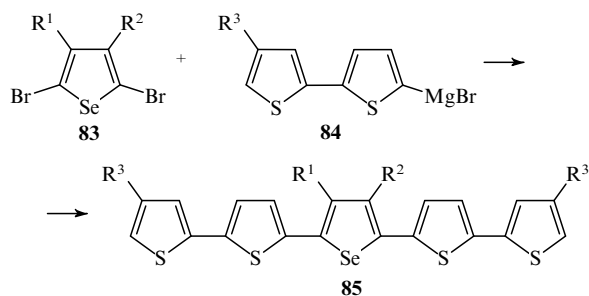
d. Certain properties of selenophenes

The photochemical [2 + 2]cycloaddition of selenophene and 3,4-dimethylselenophene to maleimide with a 1 : 1 reactant ratio leads to the monoadducts **81** in quantitative yields.²²² When a twofold excess of maleimide is used in this reaction, the bisadducts **82** are formed in 60%–70% yields. According to ¹³C NMR data, they exist in the form of three stereoisomers: *syn-anti*, *anti-anti*, and *anti-syn*.



R = H, Me.

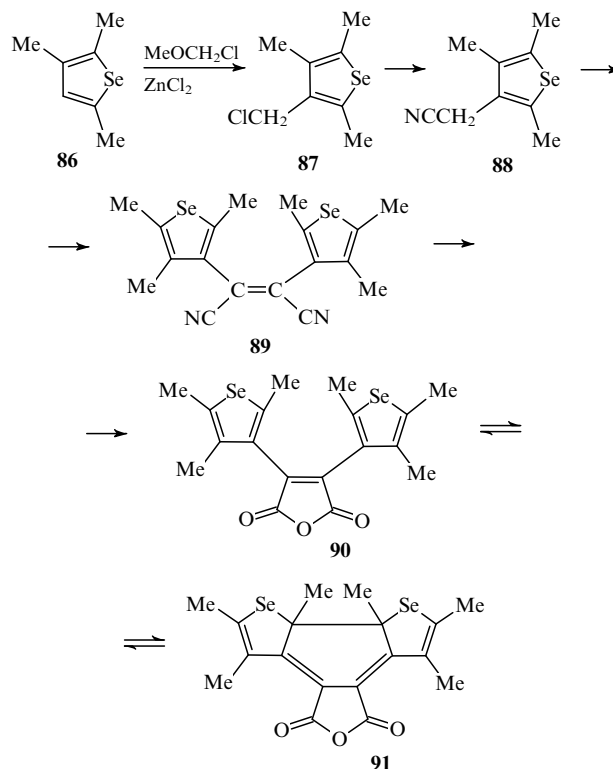
On interaction with dithienylmagnesium bromides **84**, the bromoselenophenes **83** afford the oligomeric heteroarylenes **85**.^{223, 224}



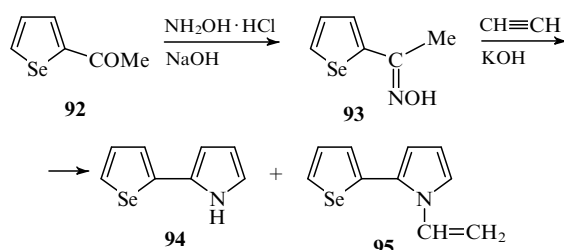
R¹, R², R³ = H, Me.

The alkylation of 2,3,5-trimethylselenophene **86** with chloromethyl methyl ether in the presence of zinc chloride has been investigated. The resulting chloromethyl derivative **87** is readily transformed into the nitrile **88**, which dimerises to the substituted ethene **89**. Treatment of the latter with KOH in aqueous EtOCH₂CH₂OH gives rise to the anhydride **90**, which on irradiation in

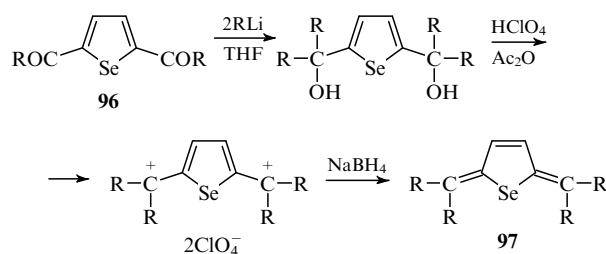
benzene at 20 °C affords a photostationary mixture with the deeply coloured cyclic form **91** capable of being fully and reversibly converted into the anhydride **90** on irradiation with light at a wavelength $\lambda > 520$ nm.²²⁵



2-Acetylselenophene oxime **93** reacts with ethyne to form a mixture of the bisheterocycles **94** (10%) and **95** (2%).²²⁶

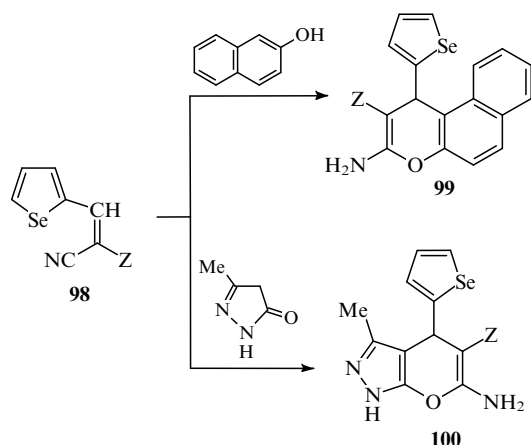


The triene heterocyclic systems **97** have been obtained from 2,5-diacetylselenophenes **96** in 46%–71% yields in accordance with the following scheme:²²⁷



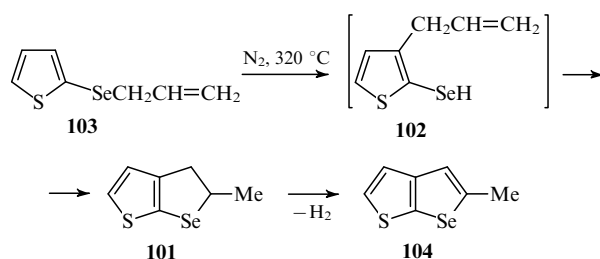
R = Ph,

The selenophene-substituted acrylonitriles **98** have been used successfully in the synthesis of the naphthopyrans **99**²²⁸ and the pyrazolopyrans **100** containing a selenophene ring.²²⁹

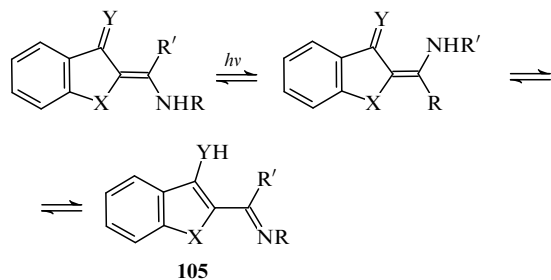


Z = CN, CO₂Et, CONH₂, CSNH₂.

2-Methyl-2,3-dihydroselenopheno[2,3-*d*]thiophene **101**, formed *via* the intermediate **102** on heating allyl 2-thienyl selenide **103**, is dehydrogenated to 2-methylselenopheno[2,3-*b*]thiophene **104**.²³⁰

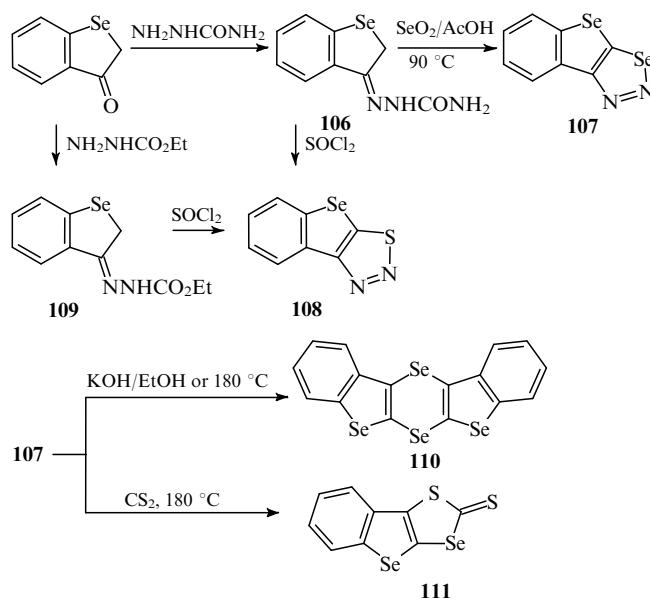


The benzenoid–quinoid tautomerism, which is a thermodynamically controlled process, has been investigated in a series of substituted benzo[*b*]heterocycles **105**. These compounds can be used for the accumulation and transformation of solar energy.^{231, 232}

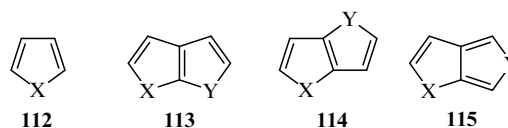


X = O, S, Se, Te; Y = O, S; R, R' = H, Alk, Ar.

Benzo[*b*]selenopheno[3,2-*d*]-1,2,3-selenadiazole **107** has been obtained in 82% yield by the reaction of benzo[*b*]selenophen-3-one semicarbazone **106** with SeO₂ in glacial acetic acid.^{233–235} Its sulfur analogue — benzo[*b*]selenopheno[3,2-*d*]-1,2,3-thiadiazole **108** — is formed on treatment with thionyl chloride of the semicarbazone **106** (yield 90%) or the ethoxycarbonylhydrazone **109** (yield 75%).^{234, 235} On treatment with an alcoholic solution of alkali, the selenadiazole **107** is converted in 94% yield into dibenzo[*b*]selenopheno[2,3-*b*:2',3'-e]-1,4-diselenine **110**, which is also formed as the sole product in the thermolysis of the selenadiazole **107** at 180 °C. On the other hand, if the selenadiazole **107** is heated at the same temperature in an autoclave in the presence of CS₂, then benzo[*b*]selenopheno[2,3-*d*]-1,3-thiaselenole-2-thione **111** is formed as the main reaction product (25%).^{234, 235}



The dependence of the transfer of the influence of the substituents in the five-membered sulfur- and selenium-containing heterocycles **112** and their annelated derivatives **113–115** on the position of the reaction centre, the nature of the heteroatom, and the type of annelation has been analysed with the aid of quantum-chemical methods and the empirical constants of the substituents.



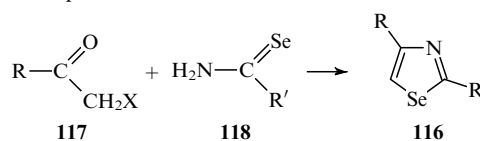
X, Y = S, Se.

In the series of isomeric selenophenothiophenes **113**, **114** (X = S, Y = Se), and **115** (X = S, Y = Se; X = Se, Y = S), it has been demonstrated by the 'pseudoatoms' method that the increase in the yield of the product of substitution in the α -position of the selenophene fragment with increase in the size of the attacking electrophile is associated with the stabilising interaction, specific to heterocycles, between the heteroatom and the attacking electrophile in the σ -complex formation stage.^{236–238} The ⁷⁷Se chemical shifts in the series of isomeric selenophenothiophenes and thienothiophenes **113–115** have also been subjected to quantum-chemical analysis and correlations have been established between the shifts and the characteristics of the distribution of electron density obtained from quantum-chemical calculations.^{238–240}

2. Five-membered heterocycles with two heteroatoms

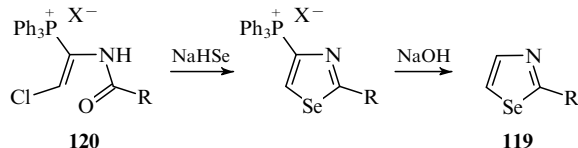
a. Selenazoles

A convenient method of synthesis of substituted selenazoles **116** is the interaction of the halo ketones **117** with compounds **118** containing a selenoamide fragment; the yields of the final products are then quantitative.^{241–248}



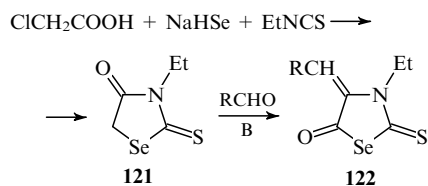
X = Cl, Br; R = Alk, Ar, Het; R' = NH₂, Alk, Ar.

A method based on the treatment of the phosphonium salts **120** with sodium hydrogen selenide has been used successfully in the synthesis of monosubstituted selenazoles **119**.^{249–253}



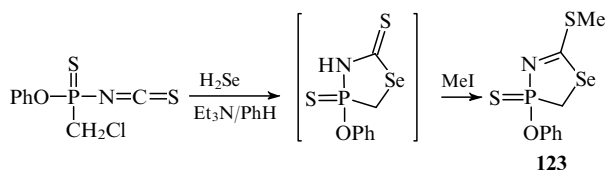
R = Alk, Ar, Het; X = Cl, ClO₄.

Sodium hydroselenide reacts with monochloroacetic acid and ethyl isothiocyanate to form the oxoselenazothione **121**. In the presence of a base, it interacts with aldehydes, forming the substituted oxothioselenazoles **122**, which are used in the synthesis of polymethine dyes.²⁵⁴

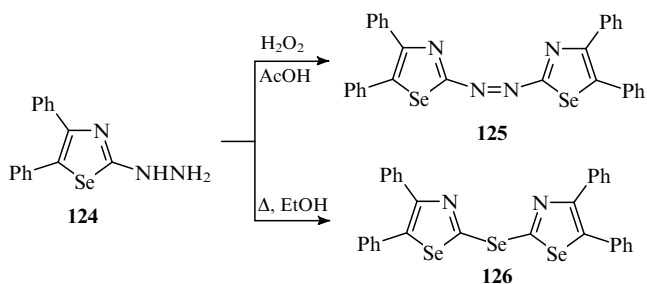


R = Ph, CH=CHPh, CH=CHC₆H₄NMe₂-4.

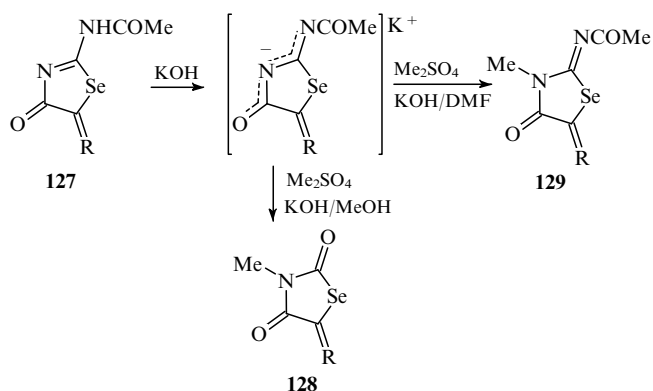
The five-membered heterocycle **123**, in which N, Se, and P atoms are present simultaneously, has been obtained in 26% yield as a result of the interaction of chloromethylisothiocyanatophosphonate with hydrogen selenide in benzene in the presence of an excess of triethylamine and subsequent treatment of the intermediate with MeI.²⁵⁵



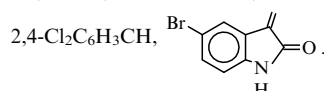
It has been reported²⁵⁶ that the azoselenazole **125** is formed on oxidation of the hydrazinoselenazole **124** with a 30% solution of H₂O₂ in acetic acid, whilst refluxing in alcohol unexpectedly afforded the selenide **126**.²⁵⁶



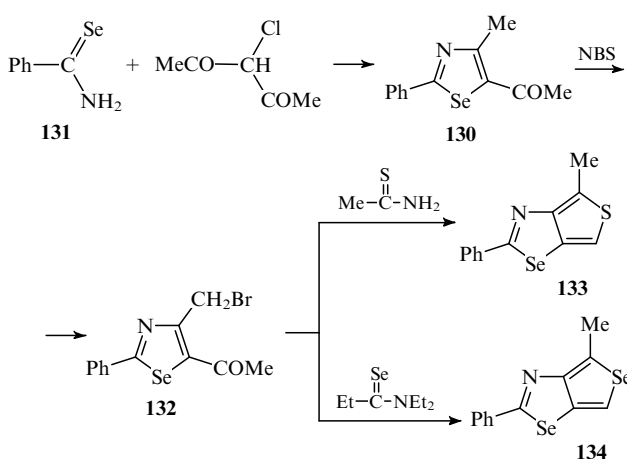
The alkylation of 2-acetamidosenazolinones **127** with methyl iodide or dimethyl sulfate in the presence of a 20% KOH solution has been investigated.^{257, 258} When the reaction is carried out in ethanol in the presence of a tenfold excess of the alkylating agent, it involves the nitrogen atom of the selenazolidine with formation of compounds **128**, while in the case where dimethylformamide (DMF) is used as the solvent, only compound **129** is formed regardless of the amount of the initial alkylating agent.



R = H₂, PhCH, 4-NO₂C₆H₄CH, 4-MeOC₆H₄CH, 2-ClC₆H₄CH,

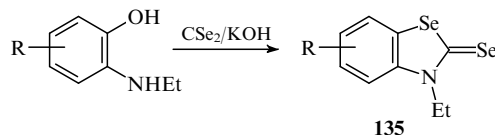


Methyl 4-methyl-2-phenyl-5-selenazolyl ketone **130**, obtained by the reaction of selenobenzamide **131** with 3-chloroacetylacetone, is brominated by *N*-bromosuccinimide with formation of the bromomethyl derivative **132**, which was used to obtain the condensed systems **133** and **134** containing the selenazole ring.²⁵⁹



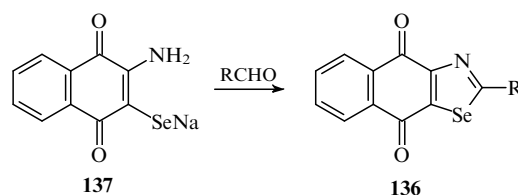
b. Condensed selenazoles

The benzoselenazoles **135**, which are used in the manufacture of photographic materials and dyes, have been obtained by the reaction of *o*-aminophenols with carbon diselenide.²⁶⁰



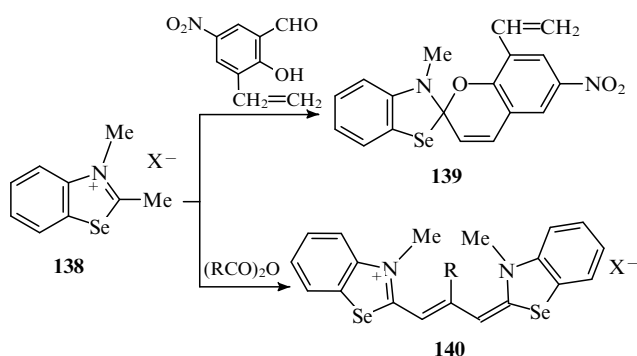
R = H, Alk, Ar, Ac, CN, OH, NH₂.

The dioxonaphthoselenazoles **136** have been obtained in 54%–68% yield by the reactions of the corresponding amino-selenolates **137** with aldehydes probably *via* a stage involving the formation of the corresponding azomethines.²⁶¹



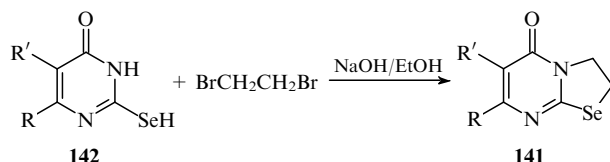
R = Alk, Ar, Het.

Among the chemical properties of benzoselenazoles, the ability of the 1,2-dimethylbenzoselenazolium cations **138** to condense with substituted salicylaldehyde to form the spiro-derivatives **139**²⁶² or with carboxylic acid anhydrides to form the selenocarboyanines **140** has been described.^{263, 264}



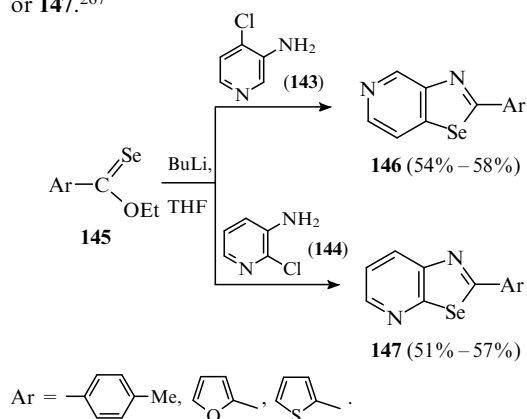
X = I, ClO₄, BF₄, OTs; R = H, Me, Et, CF₃, C₃F₇, Ph.

A promising method of synthesis of new condensed systems containing the selenazolidine ring **141**, involving the interaction of the selenols **142** with 1,2-dibromoethane, has been described.^{265, 266}

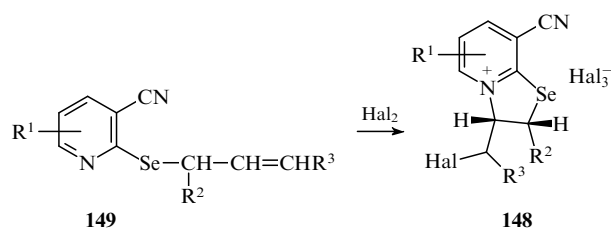


R = Me, R' = H; R-R' = (CH₂)₄.

The condensation of the chloroaminopyridine **143** or **144** with aromatic selenoesters **145** in the presence of BuLi in THF leads to satisfactory yields of the corresponding selenazolopyridines **146** or **147**.²⁶⁷

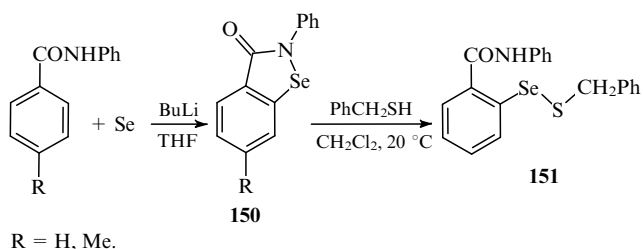


A general and convenient method of synthesis of selenazolopyridinium salts **148**, consisting in the cyclisation of substituted allyl 2-pyridyl selenides **149** on treatment with the halogens, has been developed.^{268–277} It has been shown that this reaction proceeds *via* an intramolecular electrophilic heterocyclisation mechanism and is a highly stereoselective process: *trans*-quaternisation with formation of a *cis*-junction. The stereoselectivity is ensured by the synchronicity of the interaction in the transition state of the donor (electron pair of the pyridine nitrogen atom) and the acceptor (the halogen molecule) with the multiple bond.

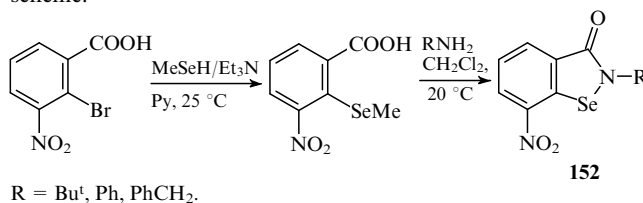


Hal = Br, I; R¹ = H, Alk, Ar, Het, OH, NH₂, CN; R², R³ = H, Alk, cyclo-Alk.

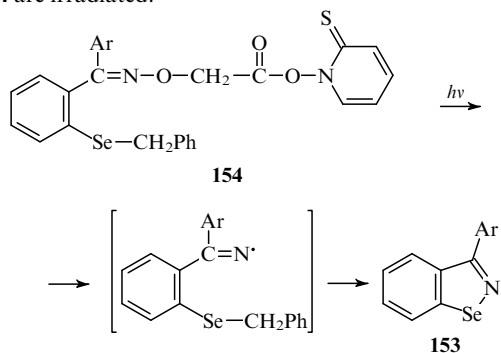
The substituted benzoisoselenazolones **150**, which possess a high antitumour activity, have been obtained in yields ranging from 20% to 60% by treating arylamides with butyllithium and powdered selenium at –40 °C.^{284, 285} On treatment with mercaptans, the benzoisoselenazole heterocycle of compound **150** (R = H) is ruptured with formation of compound **151**.²⁸⁶



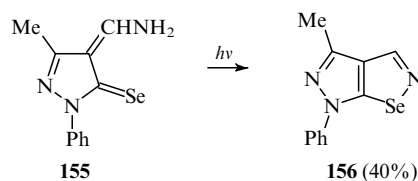
The benzoisoselenazolones **152** have been obtained from substituted benzoic acids in accordance with the following scheme:²⁸⁷



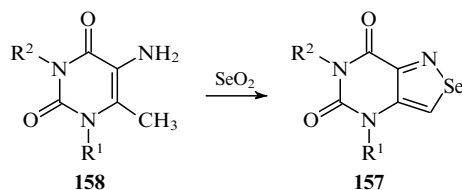
Arylbenzoisoselenazoles **153** are formed when compounds **154** are irradiated.²⁸⁸



Irradiation (λ = 330–480 nm) of the pyrazoloselenone **155** leads to a complex mixture of products, from which the condensed isoselenazole **156** was isolated in 40% yield.²⁸⁹



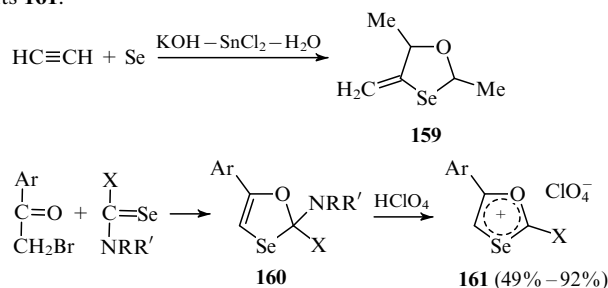
The synthesis of isoselenazolopyrimidines **157** by treating the substituted uracils **158** with selenium dioxide in dioxane at 110 °C has also been reported.²⁹⁰



R¹, R² = Me, Et, Pri, Ph.

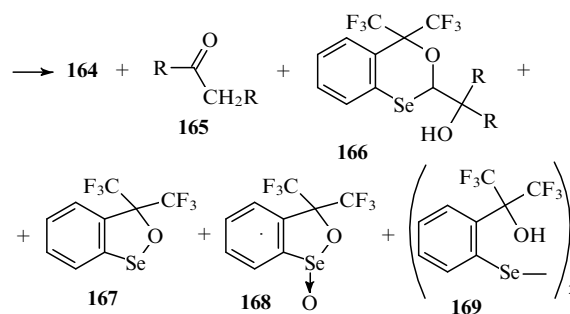
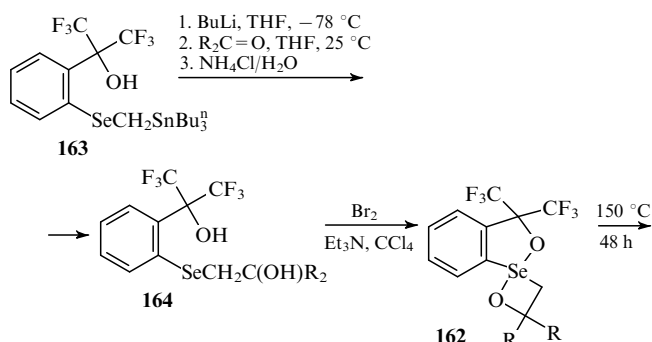
c. Oxaselenolanones

Two approaches to the synthesis of substituted 1,2-oxaselenolanones are known: the interaction of acetylene with elemental selenium in aqueous solution in the presence of tin chloride, which results in the formation of a mixture of seven selenium-containing products (one of them is 2,5-dimethyl-4-methylene-1,3-oxaselenolane **159**)²⁹¹ and the reaction of ω-bromoacetophenones with selenoamides leading to 1,3-oxaselenolanones **160**, characterised as the salts **161**.²⁹²



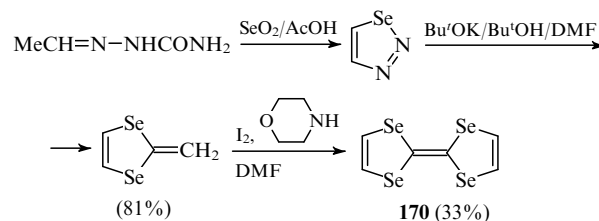
X = H, N(Me)₂, NHPh, OCH₂Ph, SPh; R, R' = H, Alk;
Ar = Ph, 4-MeC₆H₄, 4-ClC₆H₄, 4-BrC₆H₄, 4-PhC₆H₄.

The 1,2-oxaselenolane system **162** has been obtained in accordance with the following scheme: treatment of the selenide **163** with 2.4 equiv. of BuLi (THF, –78 °C, 30 min) and subsequent reaction with a carbonyl compound leads to the β-hydroxyalkyl selenide **164**. The interaction of the latter with 1 equiv. of bromine in the presence of 2 equiv. of triethylamine (CCl₄, 25 °C, 3 h) gives compound **162**.²⁹³ A complex mixture of products is formed in the thermolysis of the oxaselenolane **162**: the selenide **164** (12%), the ketone **165** (55%), the product **166** with an expanded ring (10%), the oxaselenolane **167** (16%), and 35% of a mixture of the selenoxide **168** and the diselenide **169**.

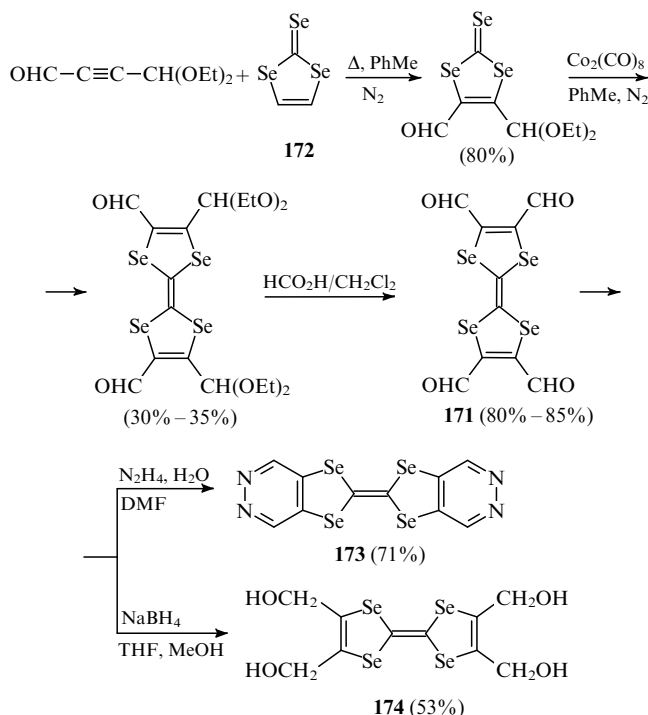


d. Selenafulvalenes

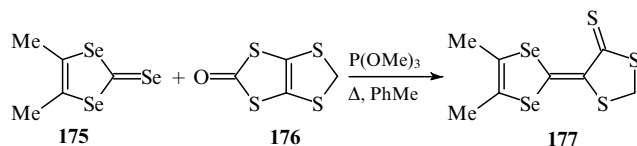
Tetrahetero(S, Se, Te)fulvalenes^{294, 295} as well as their derivatives and analogues²⁹⁶ have attracted much attention by investigators after the discovery of the conductivity²⁹⁷ and superconductivity^{297, 298} of their radical-cation salts and charge-transfer complexes. Cava and coworkers²⁹⁹ described a simple and economical method of synthesis of tetraselenafulvalene **170** by means of the following scheme:



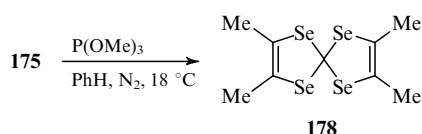
Later^{300, 301} a method of synthesis of tetraformyltetraselenafulvalene **171** from 1,3-diselenole-2-selenone **172**³⁰² was developed. It is based on the thoroughly investigated coupling reaction of 1,3-dithioles or 1,3-diselenoles.^{303–307} Treatment of the fulvalene **171** with hydrazine leads to the bispyridazino-derivative **173**^{300, 308} whilst reduction with sodium tetrahydroborate affords the tetraselenafulvalene **174**.³⁰⁰



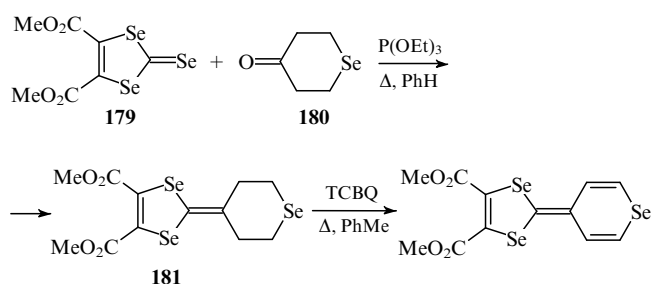
Trialkyl phosphites are used fairly widely as condensing agents for the synthesis of asymmetric selenium-containing fulvalenes.^{309–313} Thus the interaction of 4,5-dimethyl-1,3-diselenole-2-selenone **175** with the ketone **176** in boiling toluene in the presence of trimethyl phosphite under an argon atmosphere resulted in the formation of 4,5-dimethyl-2-(4-thioxo-1,3-dithiolan-5-ylidene)-1,3-diselenole **177** in 28% yield.³¹¹



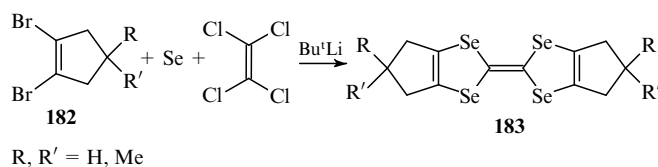
In the absence of the ketone **176**, the interaction of the 1,3-diselenole-2-selenone **175** with trimethyl phosphite in benzene at 18 °C under an argon atmosphere leads to a spiro-compound — 2,3,7,8-tetramethyl-1,4,6,9-tetraselenaspiro[4,4]nona-2,7-diene **178** — the structure of which has been confirmed by XRD data.³¹³



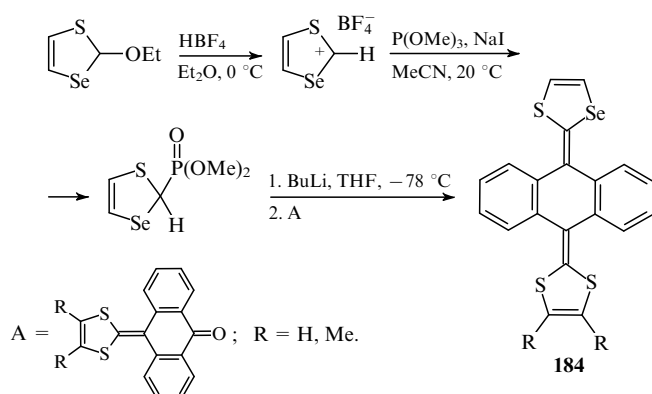
The reaction of 4,5-bis(methoxycarbonyl)-1,3-diselenole-2-selenone **179** with 4-oxoselenane **180** on refluxing in benzene in the presence of triethyl phosphite leads to the cross-coupling product **181** in 23% yield. The product is dehydrogenated on heating in toluene with tetrachlorobenzoquinone (TCBQ).³¹⁴



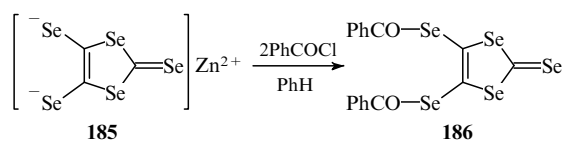
The substituted tetraselenafulvalenes **183** have been synthesized in 5%–10% yields by the interaction of the dibromocyclopentenes **182**, selenium, and tetrachloroethene in the presence of Bu^tLi.³¹⁰



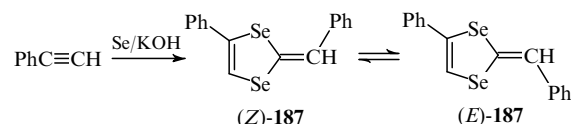
The preparation of highly conjugated selenatrithiafulvalene derivatives **184** via the following scheme has also been reported:³¹²



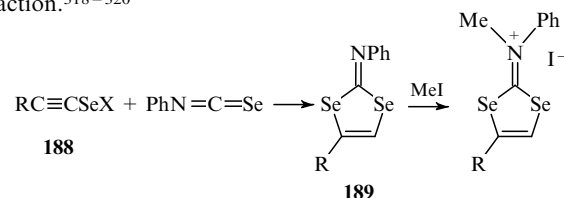
Acylation of compound **185** with benzoyl chloride in benzene leads to a 33% yield of the dibenzoyl derivative **186**.³¹⁵



A convenient method of synthesis of the substituted 1,3-diselenole **187** in the form of a mixture of isomers by the interaction of phenylethyne with elemental selenium in the presence of an aqueous KOH solution in both aprotic dipolar solvents³¹⁶ and under the conditions of phase transfer catalysis³¹⁷ has been developed.

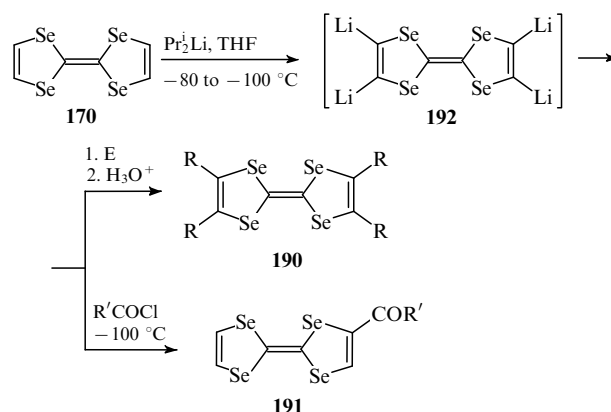


It has also been shown that the ethynylselenolates **188** enter into an anionic 1,3-cycloaddition reaction with phenyl isoselenocyanate to form the 1,3-diselenoles **189**, electron-donating substituents accelerating and electron-accepting ones retarding the reaction.^{318–320}



R = C₆H₅, 4-MeC₆H₄, 4-MeOC₆H₄, 4-ClC₆H₄, 4-NO₂C₆H₄;
X = Li, K.

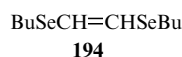
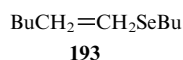
Changes permitting the synthesis of only monosubstituted tetraselenafulvalenes **191** were subsequently introduced into this reaction. For this purpose, the tetraselenafulvalene **170** is treated at –100 °C with 4 equiv. of lithium diisopropylamide in THF and the resulting tetralithium derivative **192** is then treated with a deficiency of an electrophile.³²¹



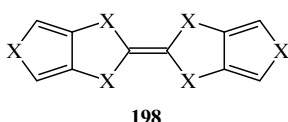
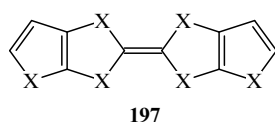
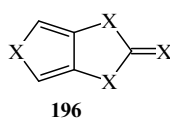
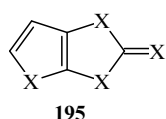
R = SPh, SePh, CO₂Me, COOH;
R' = Me, Prⁿ, n-C₁₃H₂₇, n-C₁₅H₃₁.

The metallation of the tetraselenafulvalene **170** with lithium diisopropylamide at temperatures between –80 and –100 °C followed by the addition of an excess of an electrophile (Ph₂S₂, Ph₂Se₂, ClCO₂Me, or CO₂) leads to the corresponding tetrasubstituted tetraselenafulvalenes **190**.³²²

It is of interest that treatment of compound **170** with BuⁿLi leads to the overall degradation of the molecule (only compounds **193** and **194** were detected mass-spectrometrically).³²²



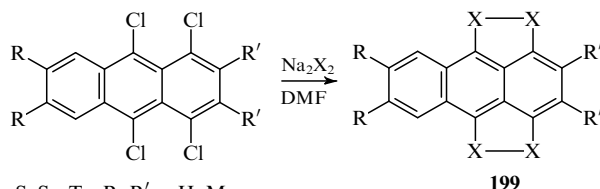
It has been shown by CNDO/CI quantum-chemical calculations with a modified set of spectroscopic parameters that heteroaromatic asymmetric thiones and selenones **195** and **196** as well as the heterofulvalenes **197** and **198** based on them have smaller ionisation potentials and energies of the lowest electronic transitions than their symmetrical isomers. An increase in the size of the thiones and selenones by their annelation to heterocyclic fragments alters the ionisation potentials and the electronic transition energies insignificantly, which can be explained by the small contributions of the atomic orbitals of these fragments to the highest occupied molecular orbital, whereupon the main contribution to the ionisation potentials comes from the $4p\pi$ orbitals of the heteroatoms in the 2,3-positions of the five-membered heterocycle as well as the $2p\pi$ orbitals of the carbon atoms forming the double bond.^{323–332}



X = S, Se.

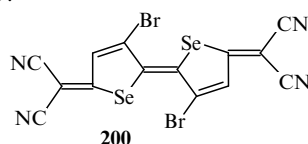
e. Other five-membered heterocycles with two selenium atoms

In order to obtain 'organic metals' with a high electrical conductivity, a method of synthesis of new types of electron donors — dimethyl- and tetramethyl-anthra[1,9-*cd*:4,10-*c'd'*]bis-1,2-dithioles and the corresponding diselenoles and ditelluroles **199** — *via* the following scheme has been developed.^{333, 334}

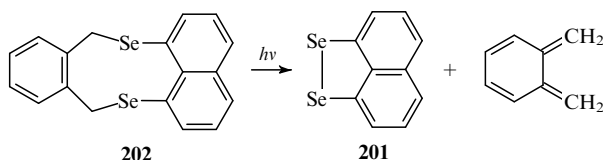


X = S, Se, Te; R, R' = H, Me.

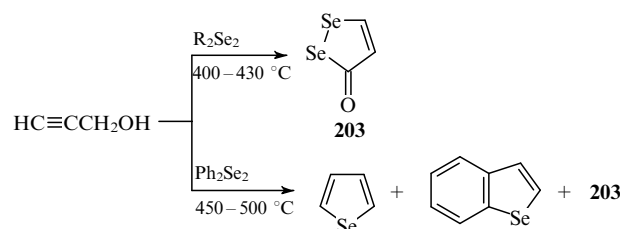
Using 7,7,8,8-tetracyanoquinodimethane as well as its 2,3,5,6-tetrafluoro-, 2,5-dimethyl-, and 2,5-dimethoxy-derivatives, 2,5-bis(dicyanomethylene)- $\Delta^{2,2'}$ -di(3-thiolene), and 3,3'-dibromo-5,5'-bis(dicyanomethylene)- $\Delta^{2,2'}$ -di(3-selenolene) **200** as electron acceptors, charge-transfer complexes with electrical conductivities ranging from 8 to $10^{-9} \text{ S cm}^{-1}$ were obtained from compounds **199**.³³³



The synthesis of naphtho[1,8-*c,d*]1,2-diselenole **201** on irradiation of 8,13-dihydrobenzo[*g*]naphtho[1,8-*b,c*]1,5-diselenine **202** has been reported.³³⁵

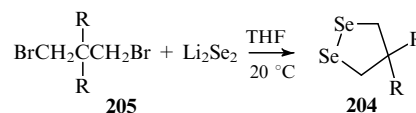


1,2-Diselenol-3-one **203** is formed in a high yield as a result of the gas-phase reaction of propargyl alcohol with dialkyl diselenides at 400 – 430°C .^{336, 337} The replacement of the dialkyl diselenide by diphenyl diselenide in this reaction lowers the yield of the diselenolone **203** and leads to the formation of selenophene and benzoselenophene together with the latter.³³⁷



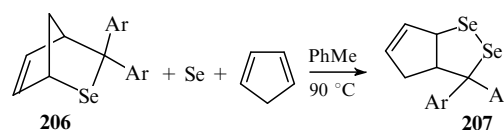
R = Me, Et, Prⁱ.

The cyclic five-membered 1,2-diselenides **204** have been obtained in a high yield (76%–98%) as a result of the treatment of 1,3-dibromoalkanes **205** with lithium diselenide in THF.^{338, 339}



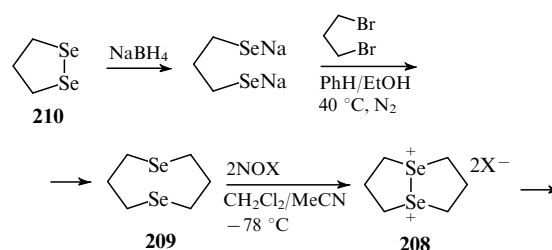
R = H, Me.

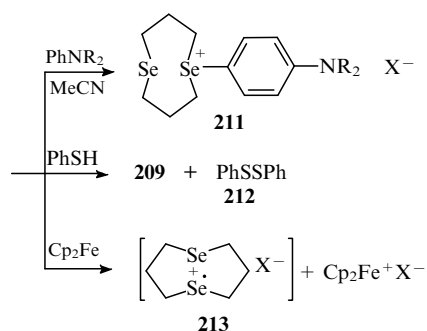
The bicyclic diselenides **207** have been obtained by treating 3,3-diaryl-2-selenabicyclo[2.2.1]hept-5-enes **206** with elemental selenium and cyclopentadiene in toluene.³⁴⁰



Ar = Ph, 4-MeC₆H₄, 4-FC₆H₄, 4-ClC₆H₄.

A series of studies have been devoted to the reactivity of the salts of the dication **208** obtained by the two-electron oxidation of 1,5-diselenacyclooctane **209** with NOPF₆ (or NOBF₄).^{341–344} The initial biselenide **209** was obtained by treating 1,3-diselenolane **210** with sodium tetrahydroborate and by the subsequent reaction of the resulting sodium propane-1,3-diselenolate with 1,3-dibromopropane in a benzene–ethanol mixture at 40°C under a nitrogen atmosphere using the high dilution technique. The interaction of the dication **208** with aniline or *N,N*-dimethylaniline in anhydrous MeCN at room temperature under an argon atmosphere leads to the corresponding *para*-substituted selenonium salt **211**, whereas the reaction with thiophenol is accompanied by the formation of the disulfide **212** (92%) and 1,5-diselenacyclooctane **209**.^{341, 343} It has also been shown that one-electron reduction with formation of the radical-cation **213** and the ferrocenium cation occurs in the interaction of the dication **208** with ferrocene in anhydrous MeCN at -20°C under an argon atmosphere.³⁴²





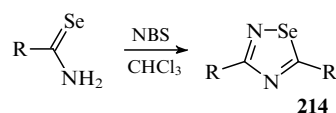
X = PF₆, BF₄; R = H, Me.

3. Five-membered heterocycles with three heteroatoms

a. Selenadiazoles

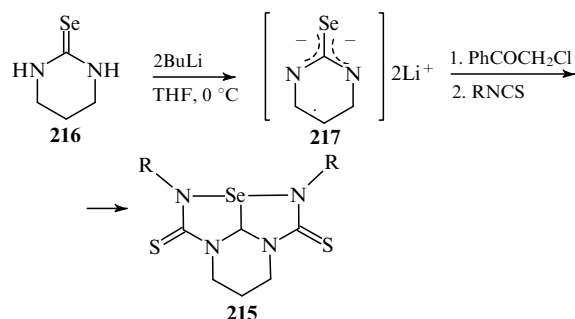
Various methods have been used to synthesise isomeric selenadiazoles.

Thus 1,2,4-selenadiazoles **214** have been obtained in 32%–87% yield by treating selenoamides with *N*-bromosuccinimide in chloroform.³⁴⁵



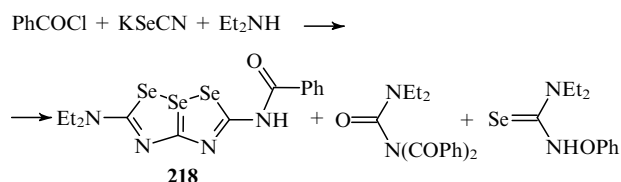
R = Ph, 4-MeC₆H₅, 4-ClC₆H₅, MeCH₂CH₂, Me(CH₂)₃CH₂, Me(CH₂)₅CH₂, Me₂N, PhCH₂S.

Condensed derivatives of 1,2,4-selenadiazoles — selenatetraazapentalenes **215** — have been obtained by treating selenourea **216** with 2 equiv. of butyllithium in THF at 0 °C under a nitrogen atmosphere and the subsequent reaction of the resulting dianion **217** with phenacyl chloride and alkyl isothiocyanate.^{346–348}

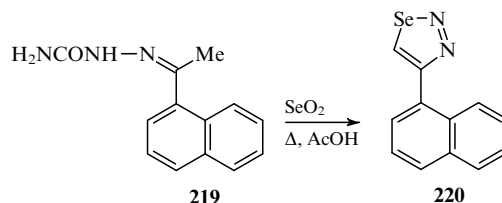


R = Me, Et, CH₂=CHCH₂.

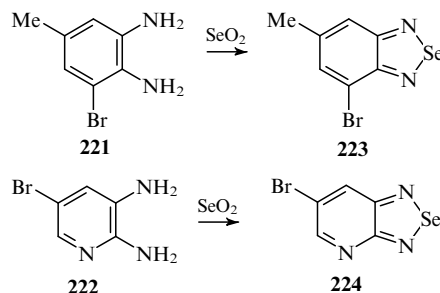
The substituted triselenadiazapentalene **218** has been synthesised in a low yield (4.8%), together with other products, by the interaction of benzoyl chloride, potassium selenocyanate, and diethylamine in acetone at room temperature.³⁴⁹



A convenient method of synthesis of 1,2,3-selenadiazoles has been developed. It consists in the treatment of the semicarbazones of aromatic and carbocyclic ketones with selenium dioxide.^{350–354} Thus treatment of the semicarbazone **219** with SeO₂ in glacial acetic acid results in the formation of 4-(1-naphthyl)-1,2,3-selenadiazole **220** in 65% yield.³⁵⁰

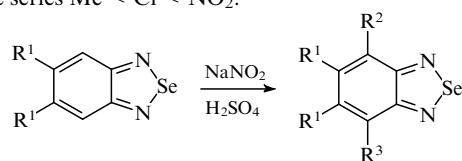


Selenium dioxide is a convenient reagent also in the synthesis of 2,1,3-selenadiazoles from aromatic and heteroaromatic diamines.^{355–358} For example, treatment of the substituted phenylenediamine **221** and 5-bromo-2,3-diaminopyridine **222** with selenium dioxide in dioxane leads to the 2,1,3-selenadiazoles **223**³⁵⁵ and **224**³⁵⁶, respectively.



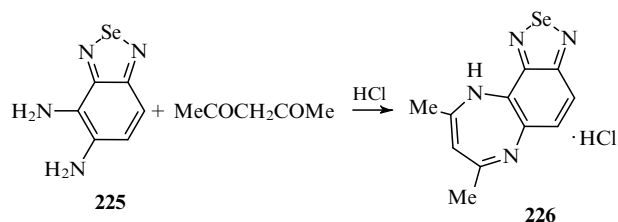
In the synthesis of condensed 2,1,3-selenadiazoles, H₂SeO₃^{359–361} and SeCl₄³⁶² have also been used as sources of selenium.

In the nitration of 5,6-disubstituted benzo-2,1,3-selenadiazoles with sodium nitrite in H₂SO₄, an increase in the deactivating influence of the substituent on their reactivity is observed in the series Me < Cl < NO₂.³⁵⁷

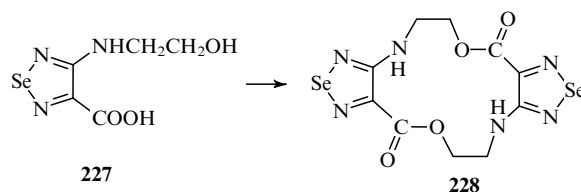


R¹ = Me, R² = R³ = NO₂; R¹ = Cl, R² = NO₂, R³ = H.

4,5-Diaminobenzo-2,1,3-selenadiazole **225** reacts with acetylacetone in the presence of concentrated HCl to form the hydrochloride of 2,4-dimethyl-1,5-diazepino[5,4-*e*]benzo-2,1,3-selenadiazole **226** in 88% yield.³⁶³



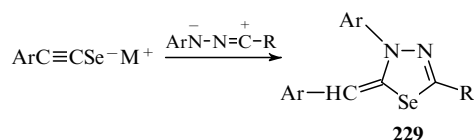
The dimerisation of 2,1,3-selenadiazole **227** to the 14-membered lactone **228** has been reported.³⁶⁴



Photoelectron He(I) spectra of benzo-2,1,3-selenadiazole and its perfluoro-derivatives have been measured and interpreted on the basis of calculations by the MNDO method, the π -fluoro-effect, and the analysis of the vibrational structure and relative

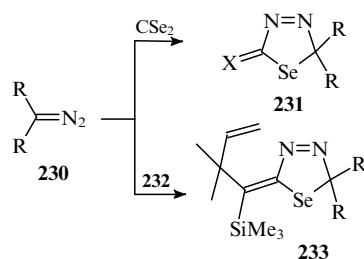
band intensities.³⁶⁵ The reduction of benzo-2,1,3-selenadiazoles with 57% HI³⁶⁶ and NaH,³⁶⁷ as well as the ability of 4- and 5-(β -amino- β -carboxy)ethylbenzo-2,1,3-selenadiazole to form complexes with Cu(II) and Pt(II) salts have been investigated.³⁶⁸

Derivatives of quaternary isomeric selenadiazole — 1,3,4-selenadiazolidines **229** — have been obtained in 70%–80% yields by the interaction of acetylenic alkali metal selenolates with nitrilimines.^{369–375}



M = Li, Na, K; R = Ar, Ac, CO₂Et.

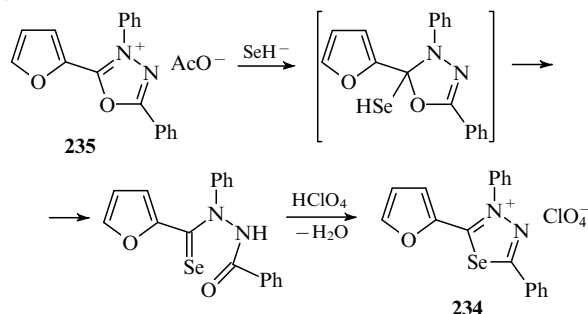
Diazoalkanes **230** react with an excess of carbon diselenide at 80 °C in toluene to form a mixture of substituted 1,3,4-selenadiazolines **231**, which have been separated by thin-layer chromatography (TLC).³⁷⁶ The introduction of selenoketene **232** into the reaction with the diazoalkanes **230** leads to a complex mixture of products, among which substituted 1,3,4-selenadiazolines **233** have been detected.³⁷⁷



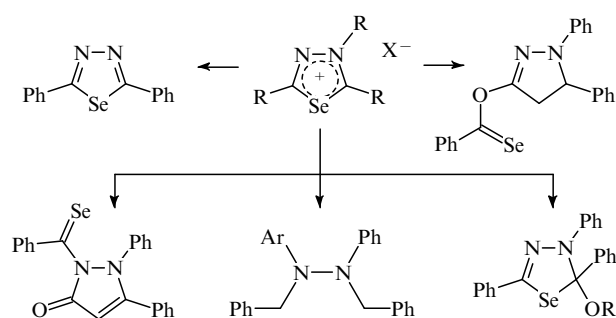
R = Bu^t, Ar; X = R₂C, R₂C=NN, RCH;

232 = CH₂=CHCM₂C(SiMe₃)=C=Se.

The 1,3,4-selenadiazolium salt **234** has been obtained by treating the oxadiazolium acetate **235** with alkali metal hydrogen selenides and subsequent acid cyclodehydration of the intermediate.^{378, 379}



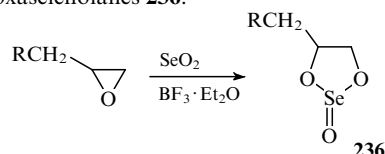
On treatment with potassium acetate in acetic anhydride, 1,3,4-selenadiazolium salts recyclise to various derivatives.^{379–382}



X = I, ClO₄, AcO, TsO; R = Alk, Ar, Het.

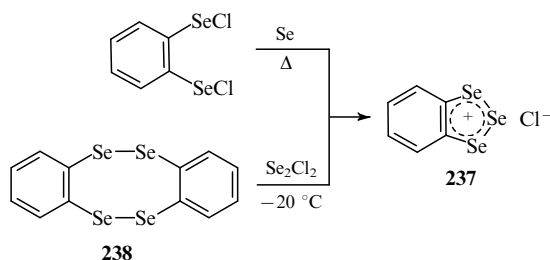
b. Other five-membered heterocycles with three heteroatoms

The interaction of equimolar amounts of selenium dioxide and epichlorohydrin or epoxyp propane in the presence of boron trifluoride etherate in dioxane at 20 °C under a nitrogen atmosphere is a convenient method of synthesis of substituted 1,3,2-dioxaselenolanes **236**.³⁸³

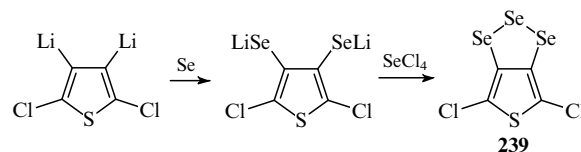


R = H, Cl.

Benzo-1,2,3-triselenolium chloride **237** has been obtained as a result of the interaction of 1,2-di(chloroseleno)benzene with elemental selenium and also by treating dibenzotetraselenocine **238** with Se₂Cl₂ in dichloromethane.³⁸⁴



Thieno-1,2,3-triselenole **239** has been obtained from 2,5-dichloro-3,4-dilithiothiophene in accordance with the following scheme:³⁸⁵

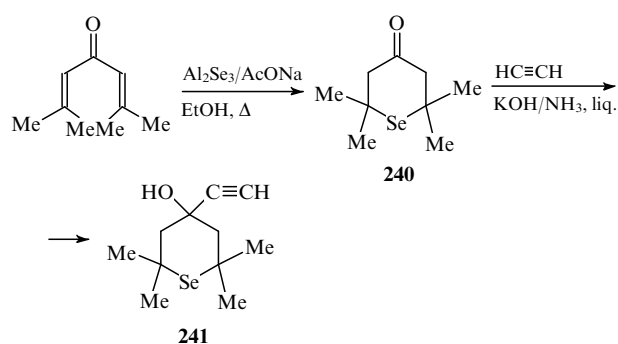


V. Six-membered heterocycles

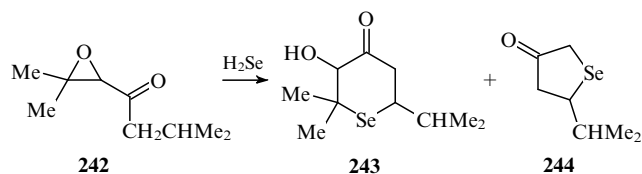
Hydrogen selenide or compounds which readily hydrolyse in the reaction medium to hydrogen selenide, as well as alkaneselenols, selenium dioxide, selenium tetrahalides, and, to a lesser extent, elemental selenium are most often used as sources of selenium in the synthesis of six-membered selenium-containing heterocycles.

1. Selenanes

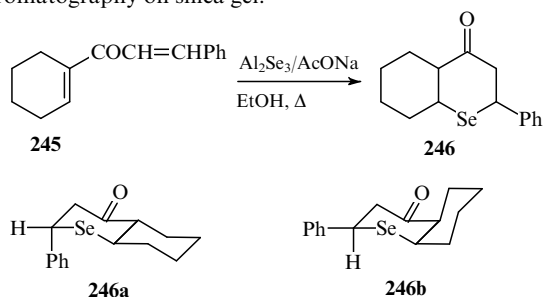
2,2,6,6-Tetramethylselenan-4-one **240** has been obtained by the reaction of phorone with a mixture of aluminium selenide and sodium acetate in 90% ethanol. Its ethynylation under the conditions of the Favorskii reaction in liquid ammonia with powdered potassium leads to the selenanol **241**.³⁸⁶



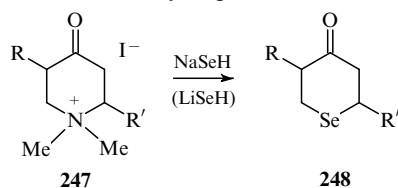
The interaction of the epoxy ketone **242** with hydrogen selenide in the presence of SnCl_4 or toluene-*p*-sulfonic acid in acetonitrile at 20 °C leads to a mixture of selenane derivatives **243** (55%) and tetrahydroselenophene **244** (12%).¹¹¹



The condensation of the dienone **245** with hydrogen selenide, formed on heating a mixture of aluminium selenide and sodium acetate in 90% ethanol, leads to 2-phenyl-1-selenabicyclo[4.4.0]-decan-4-one **246** as a mixture of four stereoisomers, from which the two individual isomers **246a** and **246b** were isolated by column chromatography on silica gel.^{387–389}

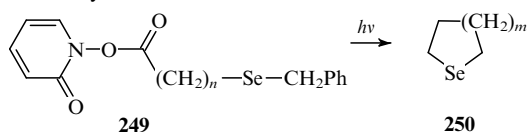


Substituted selenan-4-ones **248** have been synthesised by treating the methiodides of *N*-methylpiperidinones **247** with sodium or lithium hydroselenide in alcohol.^{390–392}



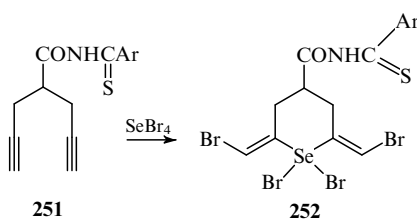
$\text{R}, \text{R}' = \text{H}, \text{Me}$.

The irradiation of a benzene solution of the selenides **249** with light from a tungsten lamp leads to the selenanes **250** in 50%–79% yields.³⁹³



$n = 3–5; m = 1–3$.

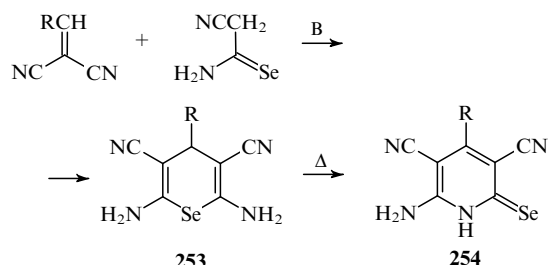
On treatment with selenium tetrabromide, compound **251** gives rise to the selenane dibromide **252**.³⁹⁴



Apart from the ethynylation of the selenanone **240** indicated above,³⁸⁶ among the chemical reactions the reduction of 2,5-dimethylselenan-4-one with lithium tetrahydroborate³⁹⁵ as well as the phosphorylation of selenan-4-one with dialkyl phosphites^{396, 397} have been described.

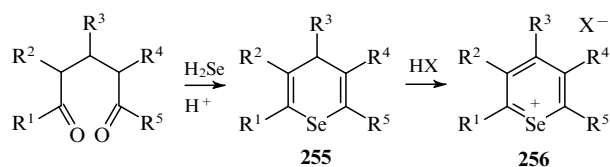
2. Selenopyrans

A convenient method has been developed in recent years for the synthesis of functionally substituted 4-aryl(heteroaryl)-2,6-diamino-3,5-dicyano-(4*H*)-selenopyrans **253**. It consists in the interaction of cyanoselenoacetamide with aryl(heteroaryl)idene-malononitriles at 20 °C in the presence of organic bases.^{398–405} On refluxing in alcohol, the selenopyrans **253** recyclise to the pyridineselenones **254**.



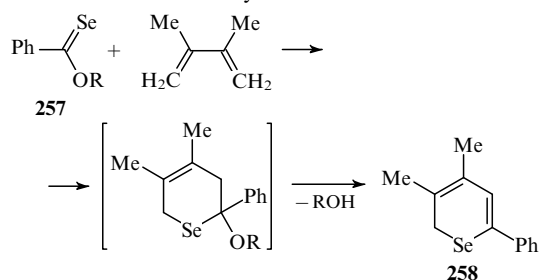
$\text{R} = \text{Ar}, \text{Het}; \text{B} = \text{HN} \begin{array}{c} \diagup \diagdown \\ \diagdown \diagup \end{array} \begin{array}{c} \diagup \diagdown \\ \diagdown \diagup \end{array}, \text{HN} \begin{array}{c} \diagup \diagdown \\ \diagdown \diagup \end{array} \begin{array}{c} \diagup \diagdown \\ \diagdown \diagup \end{array}, \text{Me}-\text{N} \begin{array}{c} \diagup \diagdown \\ \diagdown \diagup \end{array} \begin{array}{c} \diagup \diagdown \\ \diagdown \diagup \end{array} \text{O}.$

Another method of synthesis of substituted (including condensed) selenopyrans **255**, which readily form the selenopyrylium salts **256**, involves the interaction of 1,5-diketones with hydrogen selenide in acid media.^{406–413}

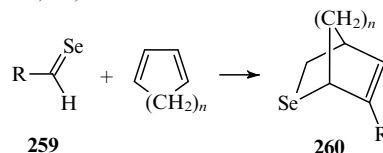


$\text{R}^1-\text{R}^2 = (\text{CH}_2)_3, (\text{CH}_2)_4; \text{R}^1, \text{R}^5 = \text{Ar}; \text{R}^2, \text{R}^4 = \text{H}, \text{Me}; \text{R}^3 = \text{H}, \text{Ar}; \text{X} = \text{Cl}, \text{BF}_4, \text{ClO}_4.$

The cycloaddition of selenocarbonyl compounds to 1,3-dienes has also been used in the synthesis of alkyl(aryl)selenopyrans.^{414–419} Thus the interaction of the selenoesters **257** with 2,3-dimethylbuta-1,3-diene leads to the 3,4-dimethyl-6-phenyl-(2*H*)-selenine **258**,¹¹⁷ while the interaction of selenoaldehydes **259** with cyclic dienes affords the bicyclic adducts **260**.⁴²⁰

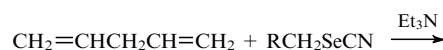


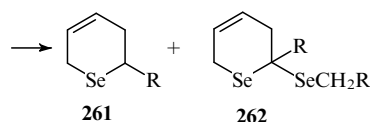
$\text{R} = \text{Et}, \text{Bu};$



$\text{R} = \text{CO}_2\text{Me}, \text{COPh}, \text{CN}; n = 1, 2.$

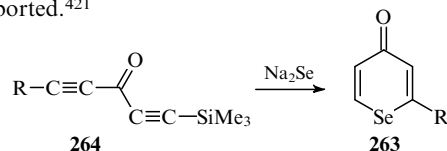
Selenocyanates react with 1,4-dienes, forming dihydroselenopyrans **261** with a small admixture of the selenides **262**.⁴¹⁹





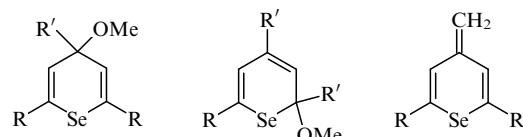
R = CN, COAr.

The synthesis of the selenopyranones **263** by the interaction of the unsaturated ketones **264** with sodium selenide has been reported.⁴²¹



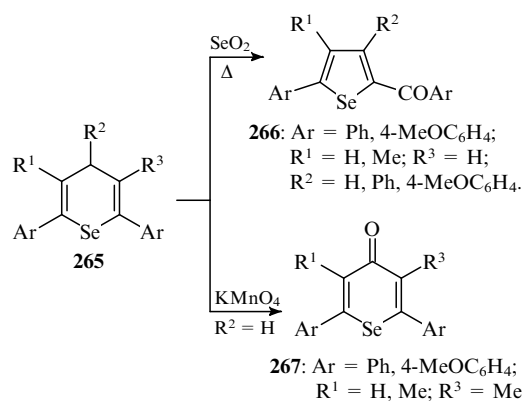
R = Ph, SiMe₃.

It has been demonstrated by ¹H NMR spectroscopy that, depending on the number and nature of the substituents in the heteroaromatic cation, the interaction of selenopyrylium salts **256** with sodium methoxide results in the formation of various reaction products: (4*H*)-selenopyrans, a mixture of (4*H*)- and (2*H*)-selenopyrans with various proportions of the isomers, or 4-methyleneselenopyrans.⁴²²



R, R' = H, Me, Bu^t, Ph, 4-MeOC₆H₄;
X = BF₄, Cl, Br.

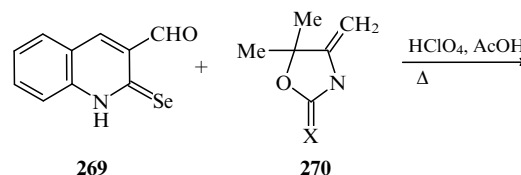
The oxidation of the selenopyrans **265** (R³ = H) with selenium dioxide in pyridine leads to the substituted selenophenes **266**.^{423, 424} On the other hand, the oxidation of the selenopyrans **265** (R² = H) with potassium permanganate in acetone or acetonitrile results in the formation of the 4-selenopyranones **267** in a high yield.^{423, 425, 426}



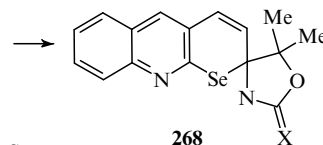
The electrochemical reduction of the selenopyrans **255**^{427, 428} as well as the dimerisation⁴²⁹ and dissociation of the salts **256** in aqueous solutions⁴³⁰ have also been investigated. In addition, a study has been made of the nucleophilic substitution in the series of selenopyrans^{422, 431, 432} and of certain other reactions.^{433–436}

3. Condensed selenopyrans

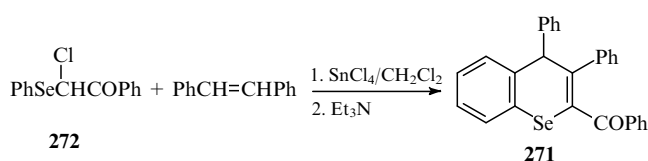
The spiro-selenopyrans **268**, incorporating a quinoline fragment condensed with the selenopyran ring, are formed when a mixture of 3-formyl-(1*H*)-quinoline-2-selenone **269** and the methylene bases **270** is refluxed in glacial acetic acid in the presence of catalytic amounts of perchloric acid.^{437–439}



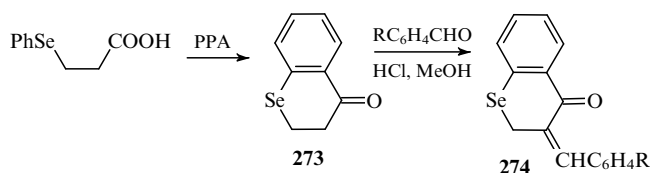
X = O, S.



The trisubstituted selenochroman **271** has been obtained by the reaction of α-chlorophenacyl phenyl selenide **272** with *trans*-stilbene in anhydrous CH₂Cl₂ at –20 °C under an argon atmosphere in the presence of zinc chloride and subsequent treatment of the reaction mixture with triethylamine.⁴⁴⁰

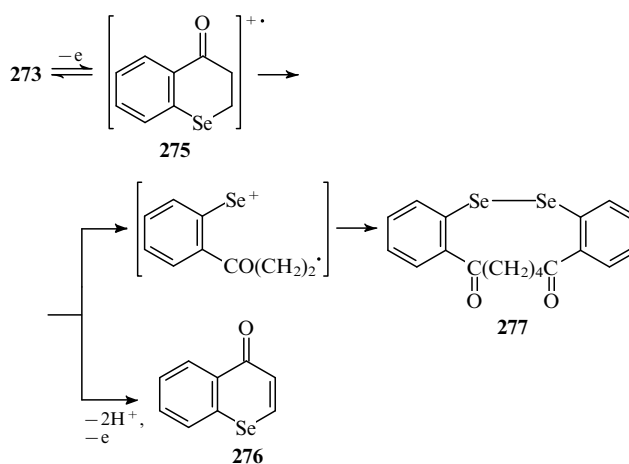


In the presence of polyphosphoric acid (PPA), 3-phenylselenopropionic acid affords the selenochroman-4-one **273**, the interaction of which with aromatic aldehydes in the presence of concentrated HCl in methanol leads to 3-arylideneselenochroman-4-ones **274** in 30%–60% yield.^{441, 442}

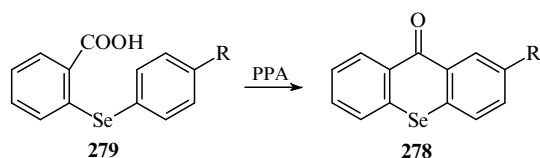


R = 4-MeC₆H₄, 4-MeOC₆H₄, 4-N(Me)₂C₆H₄, 4-ClC₆H₄,
4-BrC₆H₄, 4-NO₂C₆H₄.

Derivatives of the selenochromanone **273** are also formed from oxo-derivatives of benzo-1,3-selenazine on treatment with iron or zinc in acetic acid.⁴⁴³ The anodic oxidation of the selenochromanone **273** has been studied and it has been shown that the resulting radical-cation **275** can react *via* two parallel routes: deprotonation with formation of selenochromone **276** and homolytic dissociation of the C–Se bond with subsequent dimerisation and formation of the diselenide **277**.⁴⁴⁴

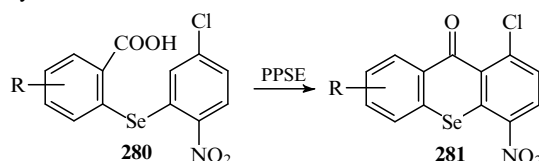


It has also been shown that the reactions of quaternised selenochromans, isoselenochromans, selenochromanones, and isoselenochromanones with Grignard reagents or metallic magnesium are accompanied by the homolytic dissociation of the C–Se bond and the formation of selenides of the benzene series.^{445,446} The intramolecular Friedel–Crafts cyclisation of 2-arylselenobenzoic acids **279** in the presence of PPA has been used for the synthesis of the selenoxanthenones **278**.^{447,448}



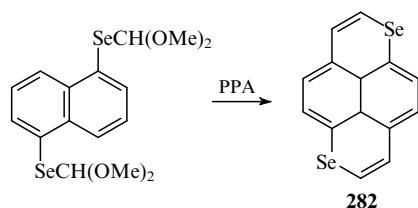
R = H, Cl.

Later a series of substituted selenoxanthenones **281** were obtained by the analogous cyclisation of the arylselenobenzoic acids **280** using trimethylsilyl polyphosphate (PPSE) as the catalyst.⁴⁴⁹



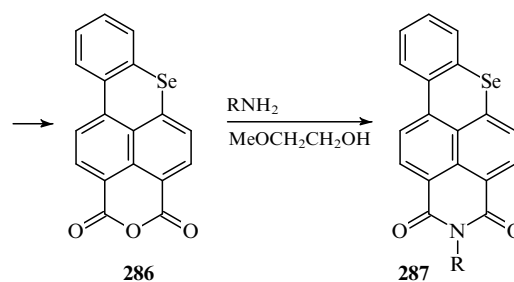
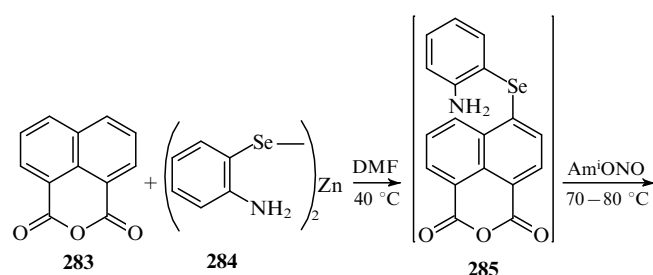
R = H, 4-MeO, 5-MeO, 3,4-OCH₂O.

Polyphosphoric acid has been used as a catalyst also in the synthesis of 1,6-diselenapyrene **282**.⁴⁵⁰



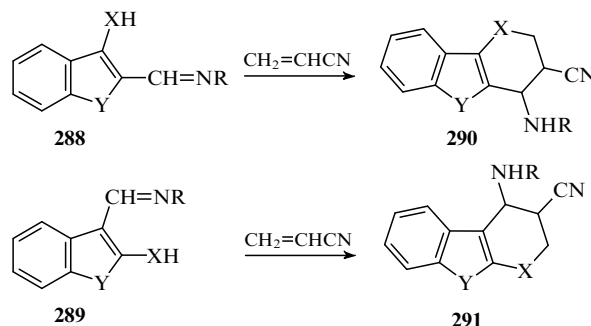
Certain properties of selenoxanthenone derivatives have been studied: carboxylation,⁴⁵¹ interaction with nucleophiles,⁴⁵² and electrochemical reduction.⁴⁵³

The reaction of naphthalic anhydride **283** with the zinc salt of *o*-aminophenyl selenide **284** in DMF leads to the anhydride **285**, which is treated, without isolation, with isoamyl nitrite and the anhydride of benzo[*k*,*l*]selenoxanthenone-3,4-dicarboxylic acid **286** is obtained in 60% yield.⁴⁵⁴ A series of imides **287** have been obtained in 64%–94% yield in the interaction of the anhydride **286** with aliphatic amines on refluxing in 2-methoxyethanol.



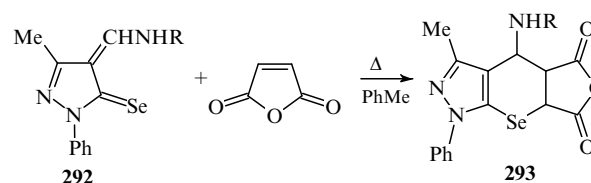
R = Bu, C₆H₁₁, C₁₈H₃₇, CH₂CH₂COOH.

Benzo[*b*]furan and benzo[*b*]thiophene thio- and selenoaldehydes **288** and **289** react with acrylonitrile to form the condensed thio- and seleno-pyrans **290** and **291** in yields up to 87%.^{455–459}



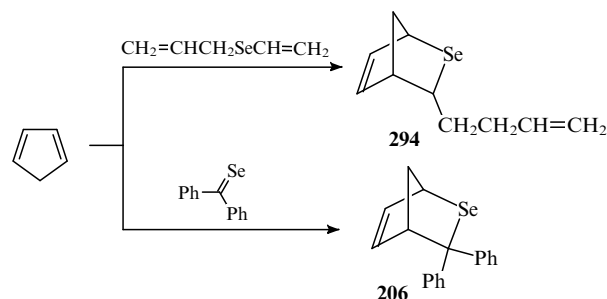
X = S, Se; Y = O, S; R = Ph, 4-MeC₆H₄, 4-MeOC₆H₄.

The cycloaddition of maleic anhydride to the pyrazoloseleones **292** on refluxing in toluene leads to the anhydrides of 4-arylamino-3-methyl-1-phenyltetrahydroselenopyrano[2,3-*d*]pyrazole-5,6-dicarboxylic acid **293** in yields up to 98%.⁴⁶⁰

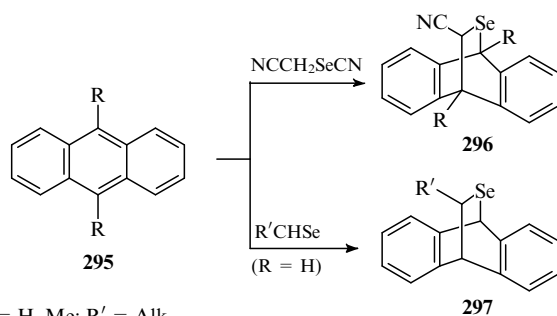


R = H, 3-MeC₆H₄, 4-MeC₆H₄, 3-MeOC₆H₄, 4-MeOC₆H₄, 3-NO₂C₆H₄.

The cycloaddition of cyclopentadiene to selenium-containing dienophiles has been used in the synthesis of bicyclic derivatives of 2-selenabicyclo[2.2.1]octene **206**⁴⁶¹ and **294**.⁴⁶²



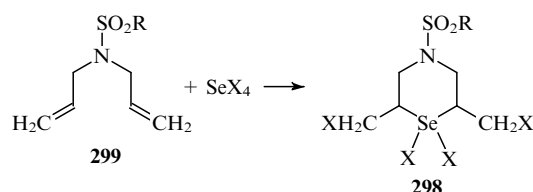
The selenopyran derivatives **296**⁴⁶³ and **297**⁴⁶⁴ have been synthesised from substituted anthracenes **295** and selenium-containing dienophiles.



$\text{R} = \text{H}, \text{Me}; \text{R}' = \text{Alk}_F$.

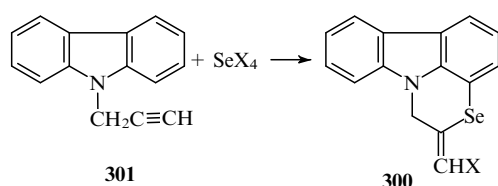
4. Six-membered heterocycles with two heteroatoms

Substituted perhydro-1,4-selenazines **298** have been synthesised by the reaction of selenium tetrahalides or phenylselenium trihalides with 1,6-heterodienes **299**.^{465, 466}



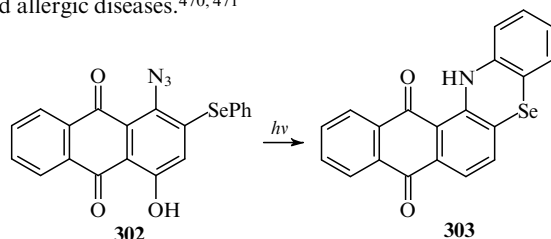
$\text{R} = \text{Ph}, 4\text{-MeC}_6\text{H}_4; \text{X} = \text{Br}, \text{Cl}$.

Selenium tetrahalides have also been used to obtain condensed analogues of 1,4-selenazines — 2-halomethylidene-1,4-selenazino[2,3-*gh*]carbazoles **300**.^{467, 468} It has been shown that the reaction proceeds *via* the electrophilic addition of SeX_4 to the triple bond and the subsequent electrophilic attack on the nucleus of the carbazole **301** with formation of the condensed system **300**.

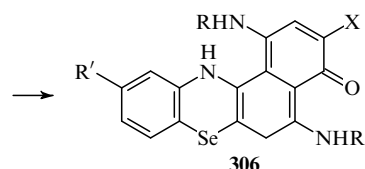
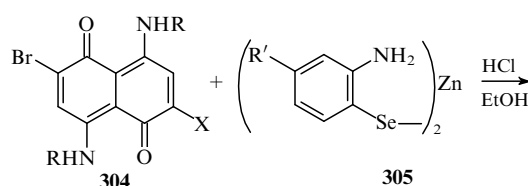


$\text{X} = \text{Br}, \text{Cl}$.

The 1,4-selenazine **303** has been obtained by irradiating the anthraquinone derivative **302**.⁴⁶⁹ Compounds suppressing the biosynthesis of leucotrienes have been detected among its derivatives; preparations based on them have been proposed for the treatment of asthma, inflammatory processes, and cardiovascular and allergic diseases.^{470, 471}

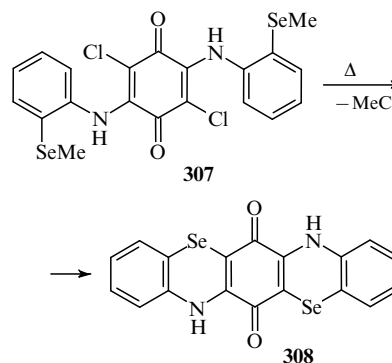


1,5-Bis(alkylamino)-(4*H*)-benzo[*a*]phenoselenazin-4-ones **306**, which absorb in the near infrared and can find application in laser techniques, have been synthesised by condensing the 1,5-naphthoquinones **304** with the zinc salts **305**.⁴⁷²

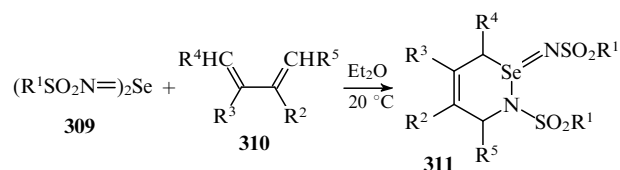


$\text{R} = \text{Me}, \text{Et}, \text{Pr}^i; \text{R}' = \text{H}, \text{Cl}, \text{OMe}; \text{X} = \text{H}, \text{Br}$.

Heat treatment of compound **307** leads to di(benzoselenazino)quinone **308** in 41% yield.⁴⁷³

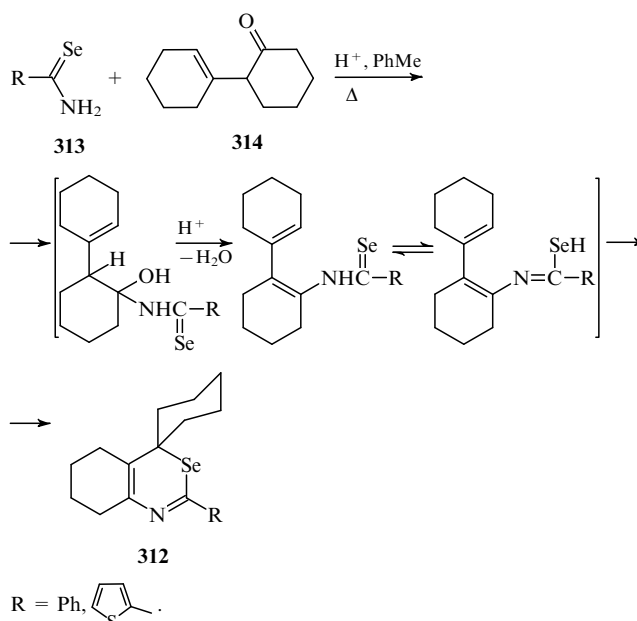


Selenium *N,N'*-di(arenesulfonyl)diimides **309** undergo [2 + 4]-cycloaddition to the 1,3-dienes **310** and afford 3,6-dihydro-1,2-selenazines **311** in 88%–94% yields.⁴⁷⁴

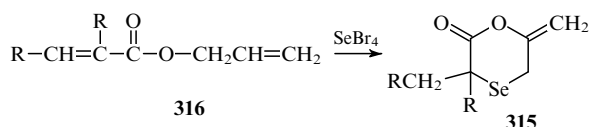


$\text{R}^1 = \text{Ph}, \text{R}^2 = \text{R}^4 = \text{R}^5 = \text{H}, \text{R}^3 = \text{Me}; \text{R}^1 = \text{Ph}, \text{R}^2 = \text{R}^3 = \text{Me}, \text{R}^4 = \text{R}^5 = \text{H}; \text{R}^1 = \text{Ph}, \text{R}^2 = \text{R}^3 = \text{H}, \text{R}^4, \text{R}^5 = (\text{CH}_2)_2; \text{R}^1 = 4\text{-MeC}_6\text{H}_4, \text{R}^3 = \text{R}^4 = \text{R}^5 = \text{H}, \text{R}^3 = \text{Me}; \text{R}^1 = \text{R}^3 = \text{Me}, \text{R}^2 = \text{R}^4 = \text{R}^5 = \text{H}$.

The 1,2-selenazine derivatives **312** have been obtained by condensing carboxylic acid selenoamides **313** with 2-(cyclohex-1-enyl)cyclohexanone **314** in the presence of catalytic amounts of naphthalene- β -sulfonic acid.⁴⁷⁵

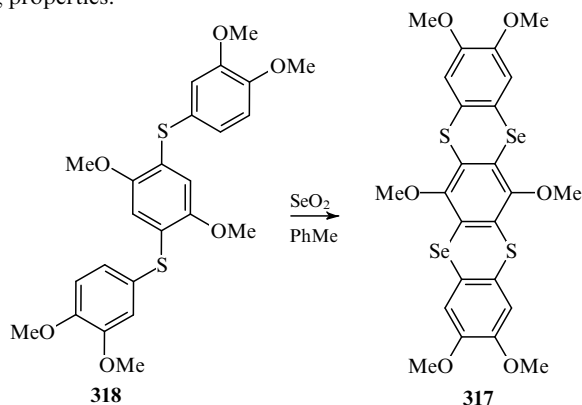


The substituted 1,4-selenoxane **315** has been synthesised by treating the ester **316** with selenium tetrabromide.⁴⁷⁶

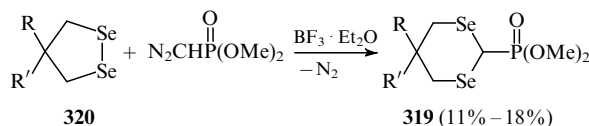


R = H, Me.

The interaction of the disulfide **318** with selenium dioxide afforded 2,3,6,9,10,13-hexamethoxy-5,12-dithia-7,14-diselena-5,7,12,14-tetrahydropentacene **317**, which possesses semiconducting properties.⁴⁷⁷

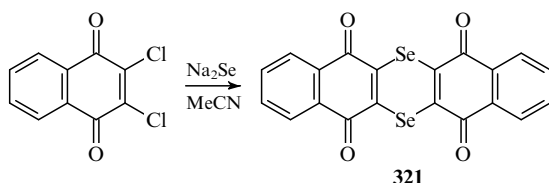


A method of synthesis of phosphorus-substituted 1,3-diselenanes **319** involving the interaction of 1,2-diselenolanes **320** with dimethyl diazomethylphosphonate in dichloromethane at room temperature in the presence of boron trifluoride etherate has been reported.⁴⁷⁸



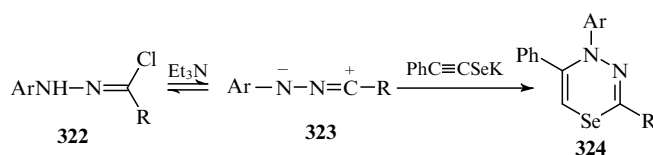
R = R' = Me; R = H, R' = Bu^t.

The condensed 1,4-diselenoxane derivative **321** has been obtained by treating 2,3-dichloro-1,4-naphthoquinone with sodium selenide in acetonitrile.⁴⁷⁹



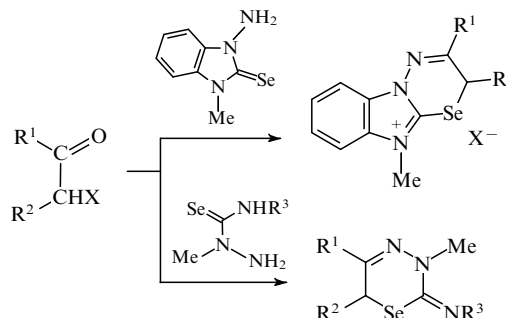
5. Six-membered heterocycles with three heteroatoms

The nitrilimines **323**, obtained by treating *N*-aryl-*C*-chlorohydrazone **322** with an organic base, undergo [3 + 3]-cycloaddition to potassium phenylethyneselenenolate, forming 2,4,5-trisubstituted (4*H*)-1,3,4-selenadiazines **324** in 89% – 100% yields.⁴⁸⁰ The interaction of the nitrilimines **323** with dialkylselenamides of mono-substituted acetic acids also leads to derivatives of 1,3,4-selenadiazines.⁴⁸¹



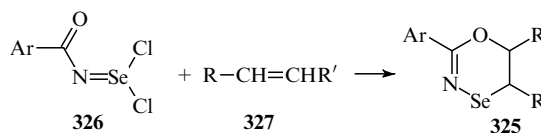
Ar = Ph, 4-MeC₆H₄, 4-BrC₆H₄; R = COMe, CO₂Et.

The reaction of α-haloketones with selenosemicarbazide, its derivatives, or other compounds containing the selenosemicarbazide fragment has been used fairly successfully in the synthesis of 1,3,4-selenadiazines, including condensed ones.^{482–487}



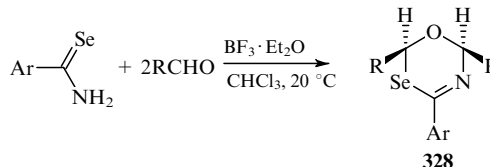
R¹, R² = H, Alk, Ar, Het; R³ = H, Alk; X = Br, Cl.

The 1,3,4-oxaselenazines **325** have been obtained by the reaction of *N*-aryliminoselenenyl chloride **326** with the alkenes **327** via the [4 + 2]-cycloaddition mechanism.⁴⁸⁸



Ar = Ph, 4-MeC₆H₄, 4-BrC₆H₄, 4-ClC₆H₄, 4-NO₂C₆H₄;
R = H, R' = Ph; R, R' = (CH₂)₄.

A stereoselective method of synthesis of 1,3,5-oxaselenazines **328** by the interaction of selenoamides with aliphatic aldehydes in the presence of boron trifluoride etherate in chloroform at 20 °C has been developed (yields 69% – 97%).⁴⁸⁹

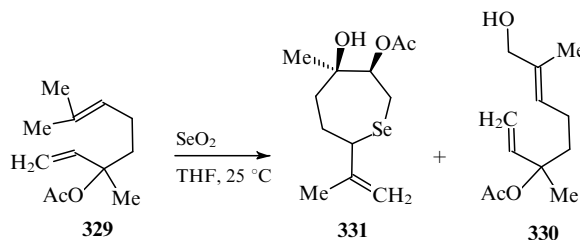


R = Me, C₇H₁₅, Bu^t, cyclo-C₆H₁₁; Ar = Ph, 3-ClC₆H₄, 4-MeOC₆H₄.

VI. Seven – nine-membered heterocycles

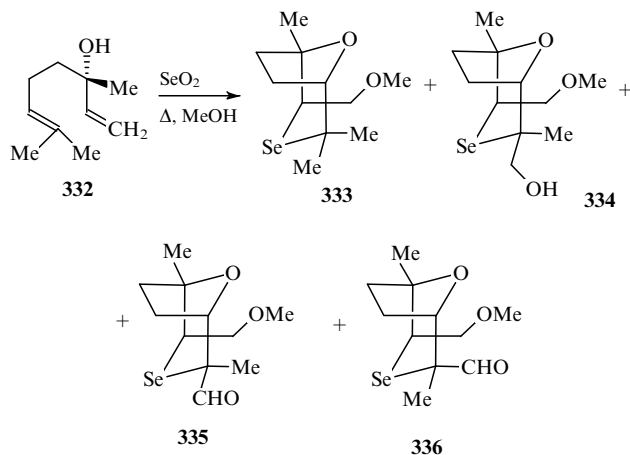
The number of publications in recent years on these selenium-containing heterocycles is small and the data presented in them are in most cases of a specific character and they are therefore described in order of increasing ring size of the heterocycle.

The interaction of freshly sublimed selenium dioxide with linalyl acetate **329** in THF at 25 °C leads to the alcohol **330** and the selenepane **331** in proportions of 7 : 3; the yield of the selenepane **331** is then 16%⁴⁹⁰ while in the case where the reaction is carried out in methanol, it is 2%.⁴⁹¹ The structure of the selenepane **331** was established by XRD.⁴⁹²

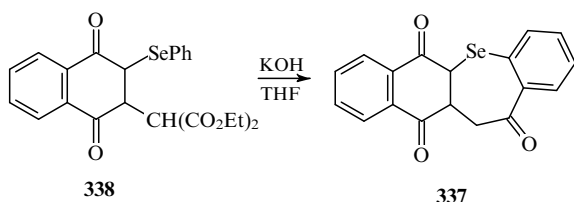


The analogous treatment of linalool **332** with selenium dioxide in methanol leads to a mixture of compounds containing the

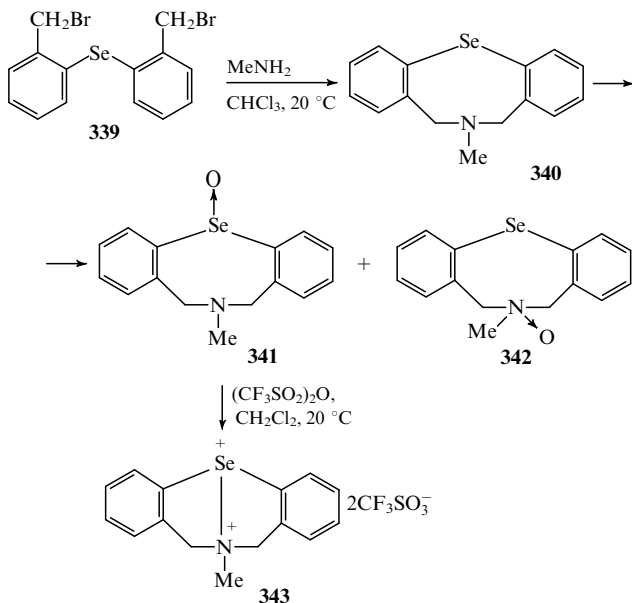
8-oxa-3-selenabicyclo[3.2.1]octane skeleton (compounds **333**–**336**).⁴⁹³ After flash chromatography on silica gel, 22.4% of compound **333**, 7.5% of compound **334**, 2.5% of compound **335**, and 3.1% of compound **336** was obtained.



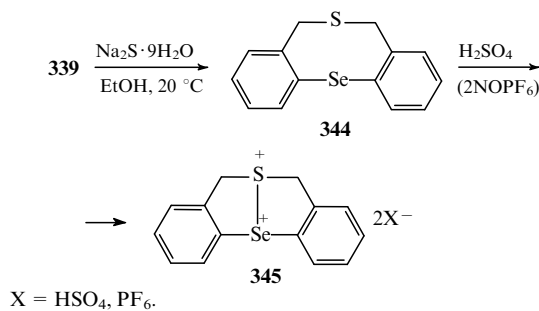
The synthesis of the tetracyclic selenenpinone **337** by the cyclisation of compound **338** on treatment with a KOH solution in THF has also been described.⁴⁹⁴



Dibenzoselenazocine **340**, the oxidation of which with *m*-chloroperbenzoic acid leads to the selenoxide **341** and the *N*-oxide **342**, has been obtained in 72% yield by the reaction of bis(2-bromomethylphenyl) selenide **339** with methylamine in chloroform at 20 °C under an argon atmosphere using the high dilution technique.⁴⁹⁵ The interaction of the selenoxide **341** with trifluoromethanesulfonic acid anhydride⁴⁹⁵ or thionyl chloride⁴⁹⁶ results in the formation of the stable crystalline salt of the dication **343**, which exists as two conformers according to ¹H NMR data obtained in deuteriochloroform at –50 °C: the boat-boat form (74%) and the boat-chair form (26%).⁴⁹⁷

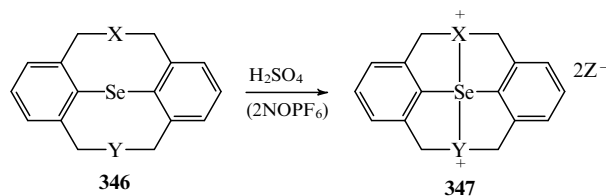


The analogous reaction of the selenide **339** with sodium sulfide in ethanol at 20 °C leads to a 90% yield of dibenzoselenathiocine **344**, which gives rise to the dication **345** on oxidation with concentrated H₂SO₄ or 2 equiv. of NO⁺PF₆[–].⁴⁹⁸



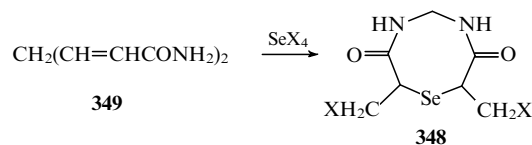
X = HSO₄, PF₆[–].

It has also been shown that salts of selenuranes **347** are formed on oxidation of dibenzodiselenocine **346** (X = Y = Se), dibenzoselenathiocine **346** (X = Y = S) or dibenzoselenazocine **346** (X = Y = NH, NCH₂Ph) with concentrated H₂SO₄ or 2 equiv. of NO⁺PF₆[–].^{499, 500}



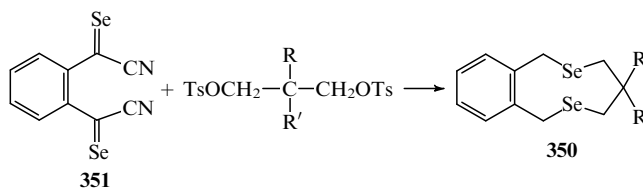
X = Y = S, X = Y = Se; X = Y = NH; X = Y = NCH₂Ph;
X = NH, Y = NCH₂Ph; Z = HSO₄, BF₆[–].

The synthesis of 2,8-dihalomethylperhydro-1,4,6-selenadiazocines **348** by the interaction of the diamide **349** with selenium tetrahalides has been reported.⁵⁰¹



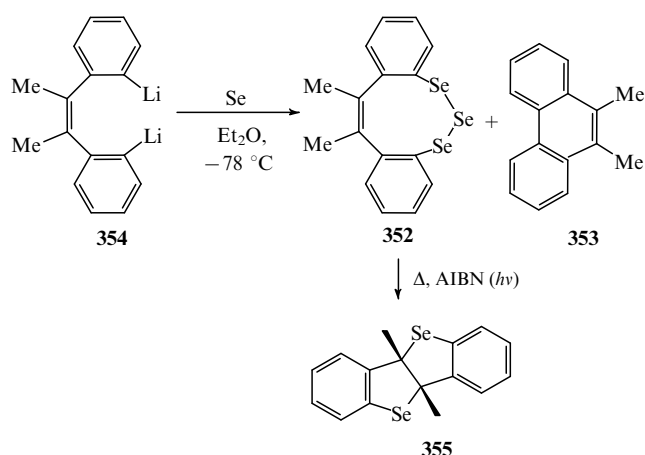
X = Br, Cl.

Nine-membered heterocycles containing two selenium atoms benzodiselenonines **350** — have been obtained by the interaction of 1,2-bis(cyanoselenocarbonyl)benzene **351** with the ditosyl derivatives of 2,2-bis(hydroxymethyl)alkanes or the corresponding cycloalkanes in THF.⁵⁰²



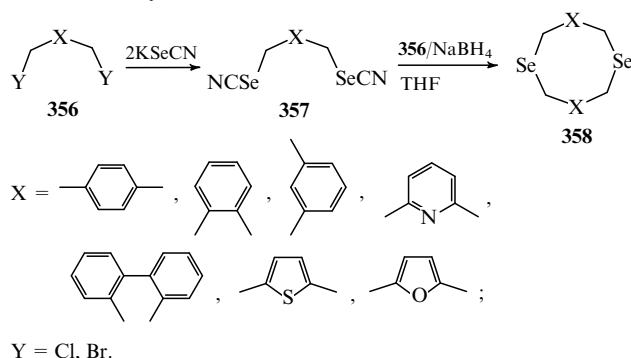
R = R' = H; R, R' = CH₂OCH₂, (CH₂)₂, (CH₂)₄.

An analogous system containing three selenium atoms — 12,13-dimethylbenzo[*d,h*]-1,2,3-triselenonine **352** — is formed in 18% yield as a mixture with 9,10-dimethylphenanthrene **353** (5%) on interaction of (*Z*)-2,3-bis(2-lithiophenyl)but-2-ene **354** with 2–4 equiv. of selenium in ether at –78 °C.⁵⁰³ On thermolysis (180 °C), on refluxing in benzene in the presence of azobisisobutyronitrile, or on photolysis (λ > 290 nm) in THF at 0 °C, the triselenonine **352** recyclises with loss of one selenium atom to 5*a*,10*a*-dimethyldibenzo[*b,f*]seleno[3,2*a*]selenophene **355**. The structures of compounds **352** and **355** were established by XRD.

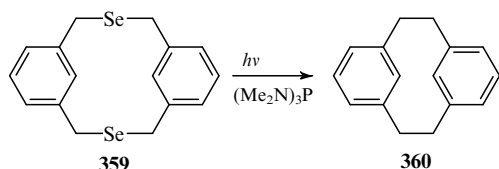


VII. Selenacyclophanes and selenium-containing crown ethers

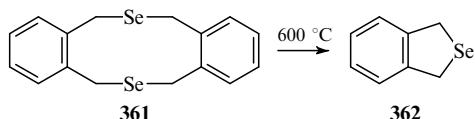
The methods of synthesis of various selenacyclophanes are based on the reactions of α,ω -dihaloalkanes or the corresponding cycloalkanes with sodium hydroselenide or potassium selenocyanate *via* α,ω -diselenocyanates, the yields of the final products approaching quantitative yields under these conditions.^{504–510} For example, bis(halomethyl)-substituted aromatic and heteroaromatic compounds **356** interact with 2 equiv. of potassium selenocyanate to form the diselenocyanates **357**, which are converted into the diselenacyclophanes **358** in a high yield as a result of the reaction with the initial halide **356** in THF in the presence of sodium tetrahydroborate.⁵⁰⁸



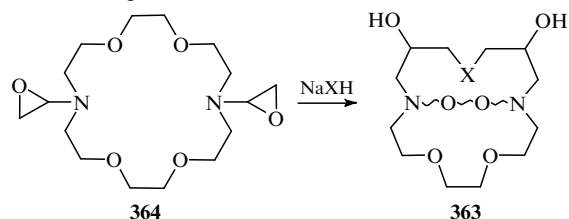
On heat treatment or photoirradiation in the presence of tertiary phosphines, the diselenacyclophanes lose selenium and are converted into cyclophanes in a high yield.^{504–507, 511, 512} For example, metacyclophane **360** has been obtained in 93% yield as a result of the photodeselenation of diselenacyclophane **359**.⁵¹³



On the other hand, 1,3-dihydro-2-benzoselenophene **362** is formed in 92% yield in the pyrolysis of 2,11-diselena[3.3]-orthocyclophane **361** instead of the corresponding cyclophane.⁵¹³

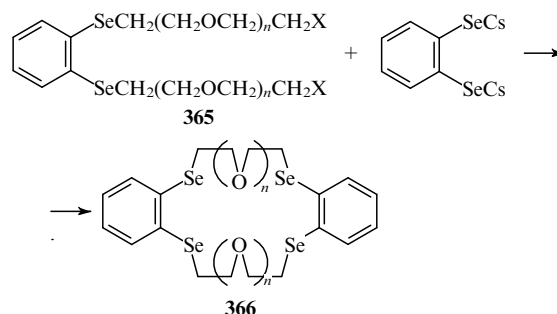


In conclusion, we shall consider data on crown ethers, cryptands and coronands containing selenium atoms and being of interest from the standpoint of the modelling of involved natural complexes. A simple method of synthesis of sulfur- and selenium-containing cryptands **363** by the interaction of bis(-methylene-epoxy)diaza-18-crown-6 **364** with sodium hydrosulfide or hydroselenide in ethanol under an argon atmosphere has been developed.⁵¹⁴



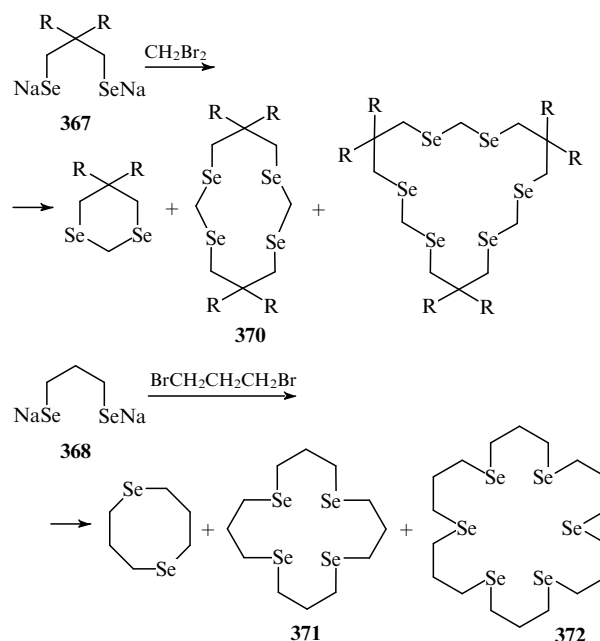
X = S, Se.

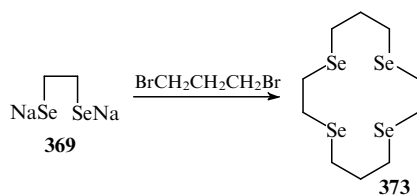
The reaction of α,ω -dihalides with cesium benzenediselenolate leads to the crown ethers **366** containing selenium atoms, in yields up to 40%.⁵¹⁵



n = 1–3; X = Br, Cl.

A new class of coronands, containing selenium atoms, has been obtained in the reactions of the sodium biselenolates **367–369** with dibromoalkanes in THF: tetraselenacyclododecane **370**, tetraselenacyclohexadecane **371**, hexaselenacyclotetracosane **372**, and tetraselenacyclotetradecane **373**.⁵¹⁶





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- ^g — *Russ. J. Gen. Chem. (Engl. Transl.)*
- ^h — *J. Struct. Chem. (Engl. Transl.)*

2-Cyanoacrylates. Synthesis, properties and applications[†]

Yu G Gololobov, W Gruber

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Abstract. Methods for the synthesis, properties and applications of alkyl 2-cyanoacrylates are surveyed. The reactions of alkyl 2-cyanoacrylates with various nucleophiles (thiols, alcohols, diols, hydrogen sulfide, phosphines, *etc.*) including a new reaction involving insertion of isocyanates and isothiocyanates into the C=C bonds in the adducts of alkyl 2-cyanoacrylates with trialkylphosphines are considered. The prospects for the use of alkyl 2-cyanoacrylates in organic synthesis, in the chemistry of polymers and in the chemistry of adhesives are described. The bibliography includes 117 references.

I. Introduction

Alkyl 2-cyanoacrylates (ACAs) were synthesised for the first time in 1949;¹ as early as 1955, it was proposed to use these compounds as one-component cold-setting adhesives.² Soon after that, industrial production of fast-curing adhesives based on ACAs started, and they appeared on the market.^{3,4}

Adhesives based on alkyl 2-cyanoacrylates are unique materials owing to two specific features. The first of them is an extremely short period needed for setting. At room temperature, surfaces can be cemented together with these adhesives over periods of several seconds, high strengths of the adhesive joints being attained fairly quickly. The second feature is that ACAs can efficiently cement together both living tissues (their use in medicine is allowed) or organic materials (plastics, rubber, wood) and inorganic materials (stones, metals, glass, porcelain, ceramics) in various combinations. Apparently, only Teflon and polyethylene provide exceptions; they can be cemented together only after treatment of their surfaces with special activators (amines, phosphines, *etc.*).^{5,6}

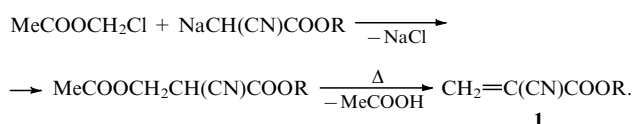
The ability of ACAs to polymerise instantaneously under the action of traces of water and various compounds (and thus to glue materials together) is the main reason accounting for the fact that up to the beginning of the 90s, only polymeric chemistry of ACAs

has developed. In fact, the monographs^{3,4} published in 1980 and reviews (see, for example, Refs 7–9) deal mostly with the polymeric chemistry of ACAs. Among monomeric derivatives of 2-cyanoacrylic acid, only esters have been described.

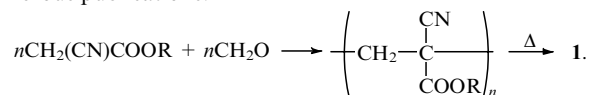
A new stage in the development of the chemistry of ACAs is associated with the synthesis of cyanoacrylic acid (CAA)¹⁰ and the involvement of this acid and its derivatives in organic synthesis.^{11,12}

II. Methods for the synthesis of alkyl 2-cyanoacrylates

Several methods for the synthesis of ACAs (**1**) are known. One of them is based on the thermolysis of alkyl 3-acetoxy-2-cyanopropionates, which are prepared from the sodium derivatives of the corresponding alkyl cyanoacetates and chloromethyl acetate.¹



However, this method has not been adequately studied. The synthesis of the compounds **1** based on the Knövenagel reaction has been developed in greater detail. This method forms the basis for the industrial manufacture of ACAs, as is illustrated by numerous publications.^{3,13–29}



It is noteworthy that depolymerisation of oligomeric ACAs formed in the first stage must be carried out under rather drastic conditions. This fact largely restricts the synthetic potential of this method (for example, it is fairly difficult to synthesise ACAs with bulky ester groups).

Among the methods developed more recently, syntheses of ACAs from methyl acrylate (**1a**),³⁰ cyanoacetylene,^{31,32} ethyl pyruvate³³ and esters of 2-cyanopropionic acid³⁴ should be mentioned [apparently, the latter method permits preparation of any ester of 2-cyanoacrylic acid, naturally except for those containing basic groups; the initial esters of 2-cyanopropionic acid can be prepared using both various aliphatic alcohols or phenols and polyols (diols, triols, tetraols) including oligomeric

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[†] The review is dedicated to William E McEwen on occasion of his 75th birthday.

slightly the standard C–C distance (1.475 Å); this implies that there is no significant conjugation between the C(1)=O and C(2)=C(3) double bonds (the length of the latter bond also coincides with the typical C=C distance equal to 1.321 Å). The lengths of the C(2)–C(4) and C(4)–N bonds are close to the standard values for molecules incorporating a C=C–C≡N fragment; in this fragment, conjugation apparently does occur.

Strong OH...N hydrogen bonds (1.88 Å) join the molecules into zigzag-like chains of the 'head-to-tail' type. The mutual arrangement of the C=C bonds of neighbouring molecules of the acid does not conform to the necessary conditions for the occurrence of topochemical reactions in the crystals of compounds with double bonds. This is in agreement with the fact that crystals of CAA are resistant to light and to prolonged exposure to X-rays.

1-Adamantylmethyl cyanoacrylate and the bis-cyanoacrylate prepared by transesterification of methyl cyanoacrylate with decane-1,10-diol have also been studied by X-ray diffraction analysis.⁴³ It was found that the molecular geometries of 1-adamantylmethyl cyanoacrylate and the bis-cyanoacrylate are similar to that of CAA. However, owing to the presence of strong electron-withdrawing groups, the methylene hydrogen atoms in these ACAs are markedly acidic, and this accounts for the short intermolecular contacts involving CH₂ groups in the crystals of these compounds.

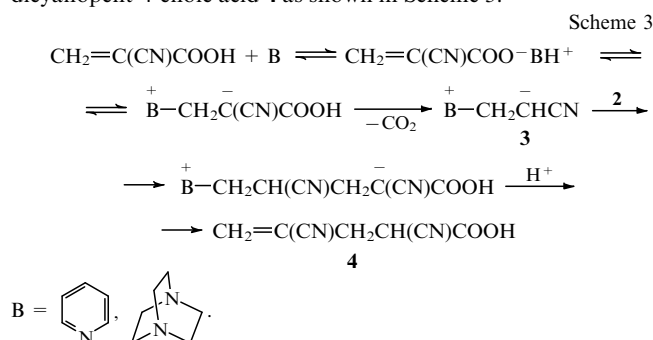
It is possible that it is the acidity of the methylene hydrogen atoms that accounts for the ready polymerisation of ACAs in the presence of nucleophiles and bases by virtue of coordination of the latter to the protons of the methylene group of ACAs.

IV. Chemical properties of 2-cyanoacrylic acid and its derivatives

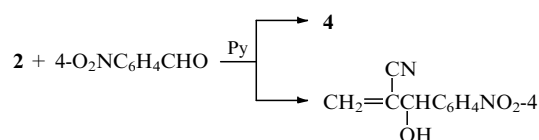
1. 2-Cyanoacrylic acid

As noted above, no reliable data about the existence of free CAA had been reported until 1985. Only Kadykov and Kochkin⁵³ described the use of CAA (without mentioning the source); however, the procedure presented by these researchers is doubtful.

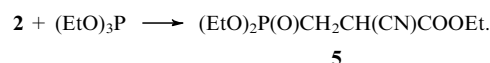
The presence of the highly electrophilic C=C bond together with the carboxyl and nitrile groups in the CAA molecule accounts for the diversity of its reactions. The preparation of CAA salts is hampered due to the strong tendency of this acid to decarboxylation and polymerisation in the presence of bases. In fact, alkalis, triethylamine and amines with non-branched radicals immediately cause its polymerisation, whereas in the presence of pyridine or diazabicyclooctane, it is rapidly converted into 2,4-dicyanopent-4-enoic acid **4** as shown in Scheme 3.⁴⁰



Obviously, in the first stage, an equilibrium is established, *i.e.* in addition to the formation of the salt, an attack by the amine on the highly electrophilic β -C atom occurs. The zwitter-ion **3** resulting from decarboxylation adds to CAA; when the reaction mixture is treated with a solution of sulfuric acid, the adduct is converted into the acid **4** in a high yield. The correctness of this reaction mechanism was confirmed by trapping the anion **3** as the adduct with 4-nitrobenzaldehyde.



Sterically hindered amines (butyldimethylamine and brucine) react with CAA to give only the corresponding salts, because steric hindrance prevents the attack on the C = C bond.⁵⁴ Conversely, in the case of triethyl phosphite, which is less basic but more nucleophilic than amines, the reaction occurs only at the double bond to give compound **5** containing a strong P – C bond.⁴⁰



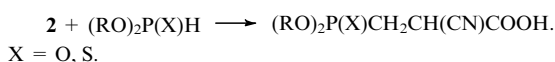
Nobody has been able yet to prepare the 2-cyanoacryloyl chloride from the acid by exchange reactions that are used successfully to convert acrylic and methacrylic acids into the corresponding chlorides. For example, CAA does not react with benzoyl chloride even at 200 °C. The reaction of CAA with thionyl chloride occurs with difficulty and stops, apparently, at the stage of formation of the mixed anhydride.⁴⁰ The chloride of CAA can be obtained only by treating the acid with phosphorus pentachloride in a mixture of toluene with xylene.⁴⁰ According to ¹H NMR data, this reaction affords an unstable adduct of the CAA chloride with HCl. When phosphoryl oxychloride and most of the toluene are removed *in vacuo*, hydrogen chloride is eliminated. The solution of 2-cyanoacryloyl chloride thus obtained can be used in various syntheses. For example, ACAs with bulky ester groups^{41,43,45} and thioesters of CAA unknown previously have been prepared from 2-cyanoacryloyl chloride. It has been found³³ that, unlike S-ethyl cyanothioacrylate which polymerises extremely easily, *S*-tert-butyl cyanothioacrylate is fairly stable. To prepare successfully esters of 2-cyanothioacrylic *S*-acid, low-polarity lead thiolate is used, because in the presence of ionic sodium and potassium thiolates, the cyanoacrylate system instantaneously polymerises, evidently, as a result of an attack by the alkali metal thiolate on the β-carbon atom at the double bond.

Like other carboxylic acids, cyanoacrylic acid smoothly reacts with trialkylchlorosilanes⁴⁰ to give the corresponding acyloxysilanes in high yields (see Scheme 2).

Unlike acrylic acid, which adds water only at 100 °C in the presence of alkali, CAA, owing to its high electrophilicity, reacts with water at room temperature. This process has been studied using deuterated water.

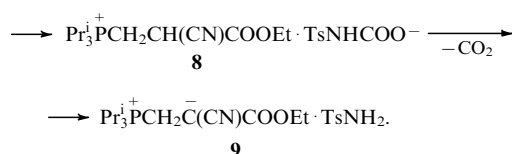
Hydration of CAA competes with its polymerisation (according to ^1H NMR spectroscopy, the latter reaction occurs much more slowly). Since the process is reversible, 2-cyano-3-hydroxypropionic acid cannot be isolated in a pure state; removal of excess water affords again free CAA and its polymeric form. Thus, the measured $\text{p}K_{\text{a}}$ value, equal to 2.3 in a 0.01 N aqueous solution, refers to an equilibrium mixture of CAA with 2-cyano-3-hydroxypropionic acid rather than to CAA itself.⁴⁰

Due to its high reactivity, cyanoacrylic acid forms adducts with acid phosphites and thiophosphites without catalysts,⁵⁵ whereas similar adducts of acrylic acid are formed only in the presence of alkaline catalysts.



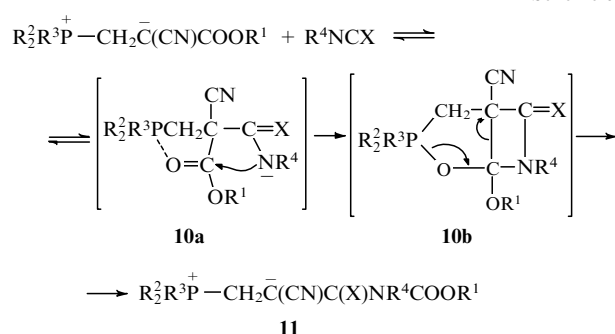
Cyanoacrylic acid dissolved in dry acetone quantitatively adds ethanedithiol present in excess to give functionally substituted bis-carboxylic acids.⁵⁶





The zwitter-ions **7** cause instantaneous polymerisation of ACAs and are readily alkylated with alkyl halides to give the corresponding phosphonium salts.⁶³ However, their interaction with isocyanates and isothiocyanates follows an unexpected pathway that includes insertion of the iso(thio)cyanate fragment into the C–C bond of the initial zwitter-ion^{62, 64–66} and leads to zwitter-ions **11** *via* intermediates **10a** and probably **10b** (Scheme 5).

Scheme 5

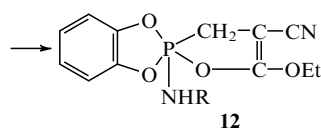
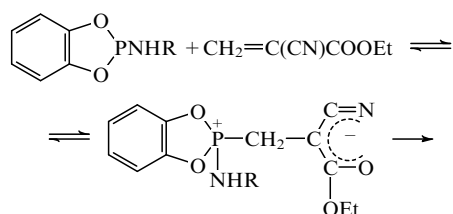


R¹ = Me, Et; R² = R³ = Prⁿ, Prⁱ, Bu, Et₂N;

R⁴ = Me, Ph; X = O, S.

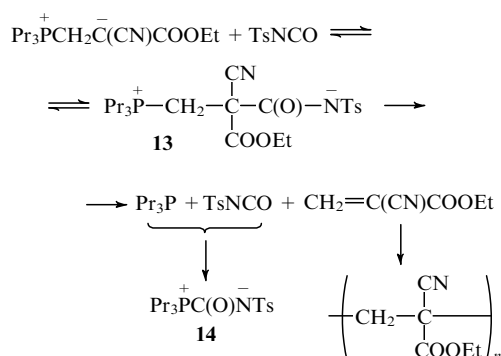
The fact that carbanions containing no phosphonium centres react with iso(thio)cyanates without changes in the carbanion skeleton⁶⁷ suggests that the rearrangement of the intermediate adduct **10a** formed in the first stage into the thermodynamically more stable zwitter-ion **11** is induced by the phosphonium centre. Apparently, its role consists in intramolecular electrophilic assistance to the attack on the carbonyl carbon atom by the nucleophilic nitrogen atom. In the limiting case, this assistance (which can be regarded as intramolecular electrophilic catalysis) gives rise to the unstable phosphorane **10b** the decomposition of which affords the zwitter-ion **11**. The structures of the reaction products (see Scheme 5) have been confirmed by IR and NMR spectroscopy; for the derivatives of methyl and phenyl isocyanate, X-ray diffraction analysis has also been carried out.^{62, 65}

The scheme for the insertion of iso(thio)cyanates includes 'opening' of the carbonyl group by the phosphonium centre. This type of reaction is well known for aldehydes and ketones,⁶⁸ but it rarely occurs for esters.⁶⁹ Therefore, to confirm the above considerations, Gololobov *et al.*⁶⁰ have studied the possibility of converting the phosphonium centre in the zwitter-ions **7** into a phosphorane structure through opening of the carbonyl in the alkoxycarbonyl group. This problem was successfully solved when ACAs were made to react with derivatives of trivalent phosphorus with a specific structure.⁶⁰ It was found that the formation of spiroposphoranes **12** can be facilitated by both steric and electronic factors. The compounds **12** in which the phosphorus atom in the five-membered ring is bound to a branched alkylamine group are the most stable.



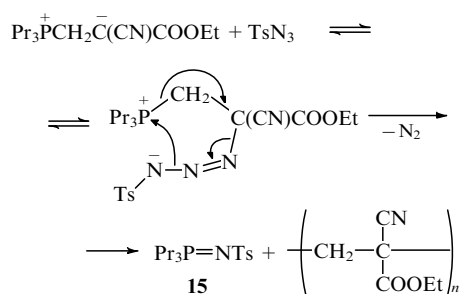
R = Bu^t, Hex.

Thus, rearrangement of the adduct **10a** into the zwitter-ion **11** depends on the nucleophilic properties of the negatively charged nitrogen atom. For example, in the case of R⁴ = Me or Ph, this atom is nucleophilic enough to attack efficiently the carboxyl carbon atom. However, when toluene-*p*-sulfonyl isocyanate is introduced into the reaction with the zwitter-ion **7**, the nucleophilicity of the nitrogen atom in the resulting adduct is relatively low and, hence, the attack on the carbon atom of the carboxyl group is inefficient. In this case, adduct **13** is stabilised *via* decomposition to give triisopropylphosphine, the initial tosyl isocyanate and the ACA. The latter rapidly polymerises, while triisopropylphosphine reacts with tosyl isocyanate to yield zwitter-ion **14**.⁶²



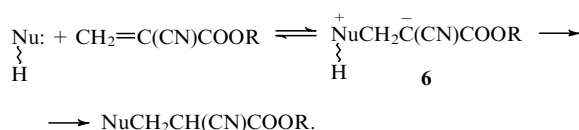
The structure of the zwitter-ion **14** was proved by X-ray diffraction analysis.⁶²

Stabilisation of the adducts arising in the reactions of the zwitter-ion **7** with organic azides is also accompanied by the liberation of an ACA molecule and yields phosphinimines **15**.⁶²

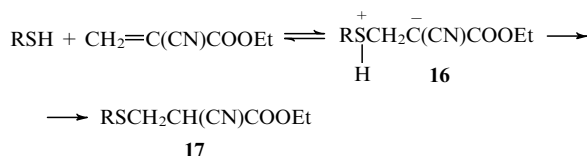


b. Reactions of 2-cyanoacrylates with nucleophiles containing active hydrogen atoms

When ACAs react with weak nucleophiles, irrespective of the particular experimental procedure, conditions are created under which ACAs instantaneously polymerise. However, when the nucleophile contains an active hydrogen atom, polymerisation of ACA is suppressed, because the primary adduct **6** is stabilised through self-protonation.



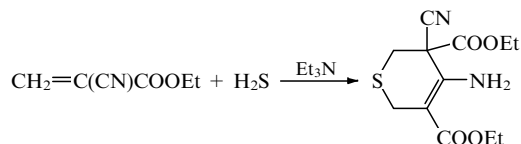
The interaction of ACAs with thiols of diverse structures under conditions when excess thiol is present (which is achieved by adding the ACA to the reactions mixture) apparently gives rise to zwitter-ion **16** in the first stage of the process. Since the proton at the sulfur atom in this zwitter-ion is relatively active, this species is rapidly self-protonated giving sulfide **17**.⁷⁰ Dithio- and thio-acids react with ACAs in a similar way.



R = Alk, Ar, HOCH₂CH₂, HSCH₂CH₂, HCl·NH₂CH₂, HCl·NH₂CH₂CH(COOH), HOOCCH₂, Ac, (EtO)₂P(S), (EtO)₂P(O).

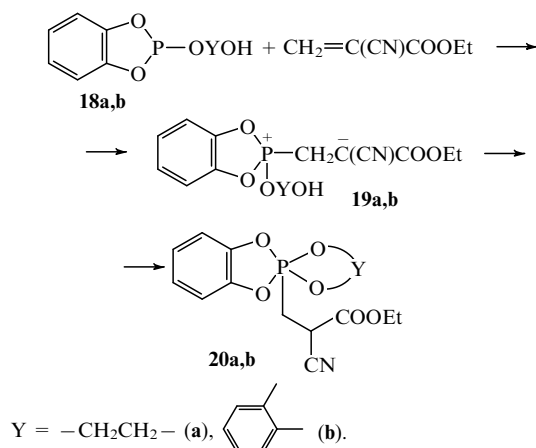
Alcohols can be introduced in this reaction instead of thiols. Normally, alcohols cause only polymerisation of ACAs, because they are less acidic and less nucleophilic than thiols; however, under special conditions (in the presence of an acid the conjugate anion of which is a weak nucleophile), formation of relatively stable adducts of ACAs with alcohols is possible.

Unlike CAA, which reversibly adds water, its esters undergo instantaneous polymerisation in the presence of water. Treatment of ethyl cyanoacrylate with hydrogen sulfide in the presence of 1% of Et₃N gives aminodihydrothiopyran **17** in a quantitative yield.



The interaction of ACAs with phosphites **18a,b** derived from pyrocatechol has been described.⁶⁰ The reaction gives rise to cyclic phosphonates **20a,b** via the corresponding zwitter-ions **19a,b** (Scheme 6).

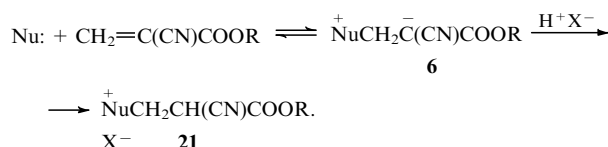
Scheme 6



In these case, too, the zwitter-ions **19a,b** formed initially undergo self-protonation.⁶⁰ It should be noted that it is the formation of five-membered phosphorus-containing rings that ensures the success of the synthesis of monomeric products according to Scheme 6. When phosphites that cannot be converted into five-membered phosphoranes like **20** are used in this reaction, oligomeric derivatives are formed.

c. Interaction of 2-cyanoacrylates with weak nucleophiles in the presence of acids

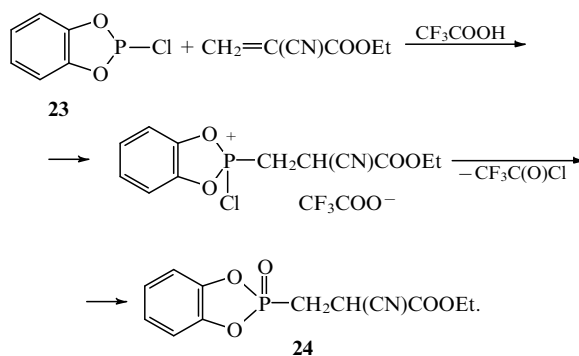
The zwitter-ions **6** formed initially in the reactions of weak nucleophiles with ACAs can also be protonated by an acid present in the reaction mixture and forming no strong bonds with the nucleophile. In this case, the reaction yields salt **21**.



In this reaction, the acid not only protonates the zwitter-ion **6**, but also activates ACA molecules. This has been confirmed by the data of IR spectroscopy,⁵⁹ according to which the nitrile and carboxyl groups in ACAs are protonated by acids, and this increases the overall electrophilicity of the ACA molecule.

The activating influence of acids ensures the occurrence of reactions of ACAs with weak nucleophiles, which do not enter into these reactions without acids. Thus 1,3,2-benzodioxachlorophosphole **23** does not react with ACAs in benzene at 20 °C; however, when the reaction mixture contains CF₃COOH, the process yields phosphonate **24** (Scheme 7).⁷¹

Scheme 7

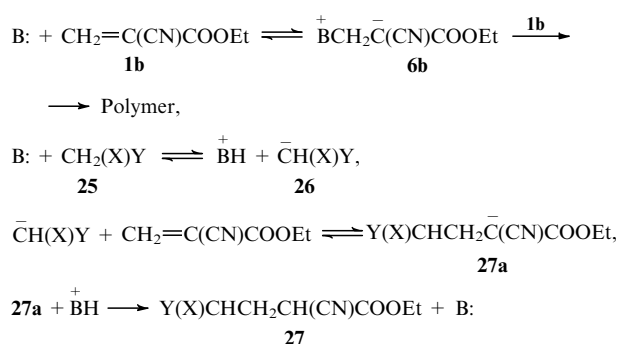


This reaction is an example of conjugate addition of a weak nucleophile and a strong acid to an ACA; the proton of the acid acts as an inductor. Alcohols and other lowly nucleophilic reagents can also enter into these reactions.⁷²

d. Interaction of 2-cyanoacrylates with CH-acids in the presence of bases

In addition to P-, S- and O-nucleophiles, C-nucleophiles (derivatives of CH-acids) can also add to ACAs under certain conditions giving rise to monomeric compounds (Scheme 8).⁷³

Scheme 8



B: — amine;

X = H, COOR (R = H, Et);

Y = NO₂, CN, Ac.

This version of the Michael reaction is possible only for those CH-acids that react with minor amounts of amines (present as catalysts of the reaction) much more rapidly than ACAs react with these amines. Thus, sufficiently basic amines (B) and relatively strong CH-acids with pK_a < 13 (for example, **25**) should be used. The acids should be rapidly converted into the conjugated bases **26**, which would either cause polymerisation of the ACA or react with the ACA to give adduct **27a**. Thus, Scheme 8 reflects a fairly complex system of equilibrium processes, the outcome of which

depends on the acidity of the CH-acid, basicity of amine B, electrophilicity of the ACA, the nature of the solvent, temperature and the order of mixing the reactants.

The results obtained in the study cited⁷³ showed that the Michael reaction involving ACAs can be used as a general method for the synthesis of esters of substituted cyanocarboxylic acids. The method is suitable for the preparation of various functionally substituted compounds.

V. Prospects for the application of 2-cyanoacrylates

Although the intense development of the 'monomeric' chemistry of ACAs has started not long ago, it has led to two important consequences. On the one hand, the chemistry of ACAs has stimulated investigation of the chemical properties of the zwitterions **7** formed by ACAs and trialkylphosphines, and this has resulted in the discovery of the insertion of the carbamide fragment into the C–C bond (Scheme 5). This, in turn, stimulated the development of a new branch of catalysis, namely, intramolecular electrophilic catalysis by a phosphonium centre. On the other hand, even the first studies on CAA and its esters provided grounds to expect that new ACAs would be synthesised, and this would markedly extend the performance characteristics of cold-setting adhesives and open up new ways for their use in industry, medicine and organic synthesis.

1. The ways to extend the temperature range of performance of adhesives based on 2-cyanoacrylates

The strength of gluing surfaces together with an ACA depends on at least two factors, all other factors being the same, namely, the adhesive capacity of the cyanoacrylate itself and on the stability of the adhesive joint under the conditions of its performance (temperature, moisture content and hostility of the medium).

Industrially manufactured methyl and ethyl 2-cyanoacrylates form high-strength adhesive joints at room temperature; however, the stability of these joints at elevated (> 80–100 °C) or low (< –100 °C) temperatures is relatively low (especially in hostile or moist media). At the same time, ample experimental material on this topic implies that the temperature range of operation of cyanoacrylate adhesives have markedly extended, and their performance characteristics have improved.

The relatively low stability of ACA polymers used under rigorous conditions can be explained by the fact that the polymer backbone contains a quaternary carbon atom (see Scheme 4). Polymers incorporating this fragment are known to possess low thermal stabilities.⁷⁴ Therefore, to increase the thermal stability of adhesive joints based on ACAs, the structure of the polymer backbone should be modified by introduction of fragments that would enhance the tolerance of the chain to high temperatures and hostile media (mostly water at various pH). The existing theoretical calculations^{4, 75, 76} provide only general recommendations on the increase in the quality of adhesives based on ACAs.

One of the possible ways of solving this problem is elaboration of cross-linked structures.⁷⁷ Two approaches to the formation of 'cross-linked' structures based on ACAs have been considered in the literature. One of them involves introduction of unsaturated carbon–carbon bonds into the ester fragment of ACAs; subsequently, these bonds ensure cross-linking of the structure.

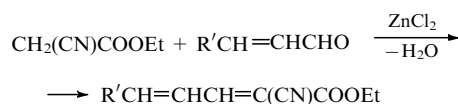
Allyl and propargyl 2-cyanoacrylates as well as other esters of CAA containing more bulky unsaturated groups have low viscosities; this is a necessary condition for attaining the interfacial contact between the adhesive and the substrate at the first stage of the formation of an adhesive joint.^{22, 46, 78–80} Under the action of traces of moisture or other active reagents, the C=C bond of the acrylate is cleaved on the surfaces being glued together.^{78, 81} Study on the thermodynamics of polymerisation of allyl cyanoacrylate and allyloxyethyl cyanoacrylate⁸² makes it possible to conclude that at room temperature these monomers are completely converted into the corresponding polymers by an anionic mechanism,

and above 100 °C, cross-linked structures are formed as a result of rupture of the multiple bonds in the allyl and propargyl fragments.^{46, 78, 79, 83} It has been noted⁸⁴ that the interfacial interaction between substrate and adhesive is due to van der Waals and dipole–dipole forces. In addition to these adhesive forces, chemical bonds of various natures (adsorption theory of adhesion) contribute to the interaction.⁸⁵ It is noteworthy that, whereas the C=C bond of the acrylate is cleaved by an anionic mechanism, rupture of multiple bonds in the ester fragment of the molecule occurs only with the participation of free radicals.⁷⁸ As a result, an adhesive joint based on unsaturated esters of CAA possesses better performance characteristics than a similar joint based on saturated derivatives.^{46, 86} The main drawback of cross-linked structures based on unsaturated 2-cyanoacrylates (regarding their practical use) is that in this case, strengthening of adhesive joints occurs only at elevated temperatures (> 100 °C). However, it is often necessary that joints be strengthened below 100 °C. In addition, this procedure can yield a rigid cross-linked polymer and, consequently, the adhesion layer can become brittle.⁷⁹ Elastomers can be partly dissolved in ACAs during gluing to give interpenetrating networks⁸⁷ (the process is described in terms of the diffusion theory of adhesion). The second approach to the production of a cross-linked adhesive layer is based on copolymerisation of methyl or ethyl cyanoacrylates with unsaturated compounds of various types. Apparently, by selecting an appropriate comonomer, one can obtain adhesive joints with properties varying over a wide range. This approach is more advantageous, because in some cases, a 'cross-linked' adhesive joint can be obtained at low temperatures. Unsaturated compounds containing electronegative polar groups have been used as comonomers, because, on the one hand, owing to these groups, compounds enter in the copolymerisation with ACAs and, on the other hand, these substituents ensure additional cohesion with the substrate. This line of research has led to impressive progress.^{3, 4, 87–95} Evidently, the structure of 2-cyanoacrylates derived from diols³⁷ and triols⁹⁶ is nearly ideal, because in these cases, a cross-linked adhesive joint is formed rapidly under conditions close to those used for the polymerisation of the main monomer. Unfortunately, at present, it is fairly difficult to produce bis- and tris-cyanoacrylates in large amounts. Some methods proposed for their synthesis^{34, 37} are labour-consuming and expensive; direct esterification of CAA^{41–43} or its chloride as well as transesterification of methyl cyanoacrylate with diols³⁹ can be used only on a laboratory scale.

Judging by several publications,^{77, 97–103} the research aimed at the involvement of esters of 2-cyano-2,4-pentadienoic acid in the copolymerisation with ACAs is proceeding vigorously. The derivatives of ethylene glycol and 2-cyano-2,4-pentadienoic acid are especially efficient.⁷ These esters polymerise at room temperature in the presence of the same catalysts that induce polymerisation of ACA to give a cross-linked structure. It has been shown^{77, 97} that the performance characteristics of ACAs are markedly improved when they are used as mixtures with butadiene derivatives.

These cross-linking reagents are synthesised by the Knövenagel reaction between the corresponding esters of cyanoacetic acid and aldehydes (Scheme 9).^{98, 99}

Scheme 9



R' = H, Me.

A significant feature of the process shown in Scheme 9 is that anhydrous zinc chloride dissolved in dioxane or THF is used as the catalyst. A method for the synthesis of bis-2-cyanopentadienoates derived from diols containing disiloxane units in the chain has been recently described in a patent.¹⁰²

2. The use of 2-cyanoacrylates in medicine

The ability of ACAs to polymerise on the surface of a living tissue over periods of several seconds under very mild conditions without special initiation permits these compounds to be regarded as promising surgical materials.¹⁰⁴ It is of prime importance that the polymer based on an ACA is destroyed relatively quickly in a living organism.¹⁰⁵ Polymers based on isobutyl and isoamyl cyanoacrylates are highly biocompatible. It should also be mentioned that ACAs are relatively non-toxic and possess antimicrobial activities. 1,2-Isopropylidene-glyceryl cyanoacrylates are quite promising in this respect.²⁰ Laboratory and clinical tests on the regeneration of tissue cells and restoration of other characteristics of an organism have shown that ACAs ensure strong and elastic connection of tissues; simultaneously, they exhibit antiseptic properties and pose no harmful consequences.¹⁰⁵ Medical adhesives of this type are used during surgical operations on lungs, brains, heart, kidneys, on organs of digestion, sight and respiration, bone tissue and teeth.^{3, 4, 106–109} Efficient medicinal adhesives of the MK series and SO-9m, SO-9t and SO-57 trademarks prepared using fluorinated methacrylates as comonomers have been developed in the former USSR by Russian, Ukrainian and Azerbaijanian chemists. These formulations are non-toxic and tolerant to disinfectants.¹¹⁰ They possess bacteriostatic and bactericide properties; besides, they are biodegradable in an organism and form no toxic products of decomposition. They also cause no immunological reaction.¹¹¹

The second way of using ACAs in medicine is associated with the development of medical preparations of prolonged action based on them. A procedure has been elaborated for incorporating medical preparations into an ACA-based polymeric matrix. When an ACA is introduced into an intensely stirred solution of a drug, it polymerises to give particles with a size of 170–350 nm containing molecules of the drug sorbed in the polymeric matrix. This procedure was used to obtain immobilised apomorphine¹¹² and oxytocin.¹¹³ The procedure is general and, apparently, it can be used in several variants.

3. Other applications of 2-cyanoacrylates

Polymers based on ACAs are used to produce photo- and electrono-resists. By chemical deposition of perfluoroethyl cyanoacrylate vapour on a support, a photoresist with a sensitivity of 0.2 J cm^{-1} has been obtained.¹¹⁴ Positive electrono-resists have been obtained using homopolymers of ACAs and their copolymers with functionally substituted monomers.¹⁰⁸ Lengthening of the hydrocarbon chain in the ester group of ACAs markedly decreases the adhesive properties of these compounds. Alkyl cyanoacrylates in which the alkyl chain consists of more than six methylene units have found application in the formation of Langmuir–Blodgett monomolecular layers.¹¹⁵ Monolayers are formed by polymerisation of CAA esters (from hexyl to decyl ester) directly on the water surface. Since the energy of interaction of the cyano-group in the polymer with water is relatively low (14.6 kJ), the monolayer can be easily transferred on a solid support. At the same time, monomolecular layers of poly(alkyl cyanoacrylates) exhibit some adhesion both to hydrophilic and to hydrophobic surfaces. The above technology for the preparation of Langmuir–Blodgett films can be used in the production of micro-instruments by the submicron technology.

Cyanoacrylates are readily soluble in liquid carbon dioxide;¹¹⁶ therefore, ACAs packed in aerosol bottles can be used in those cases where a high concentration of ACA vapour is needed. It is clear that the aerosol use of ACAs would help to solve some unexpected problems, because it would permit almost instantaneous production of a polymeric adhesive surface on various objects. ACA vapours deposited on various surfaces polymerise on them and thus fix any traces left there, for example, fingerprints.¹¹⁷

* * *

The data presented in this review provide grounds for believing that at present, a new stage in the development of the chemistry of ACAs has started. This can lead to development of cold-setting adhesives with better performance properties; in addition, new applications of CAA derivatives can appear, and the use of ACAs in organic and organometallic synthesis can become wider.

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The role of topological disorder in the physical chemistry of polymers

Yu A Shlyapnikov

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Abstract. The topological disorder, which consists of a set of diverse knots, folds, and entanglements of polymer chains, determines many properties of a polymeric substance. It is manifested in processes involving the sorption of low-molecular substances by the polymer and in the chemical reactions of the substances dissolved in the polymer. The bibliography includes 59 references.

I. Introduction

Zones with a relative degree of order in the disposition of monomer units (short-range order), which alternate with zones where this order is violated, are known to exist in real polymers. The zones with disturbed order arise around topological structures such as loops, folds, various entanglements of the polymer chains (see, for example, Yeh¹), and also at the ends of macromolecules. The majority of zones of short-range order violation [units of disorder (UOD)] are formed in the synthesis of the polymer or during its precipitation from solution and are retained throughout the existence of the given polymer sample, not disappearing even on melting. The set of diverse UOD is referred to as the stable topological disorder, which determines many properties of the polymer.^{2,3} According to the present author, the degree of topological disorder is the missing parameter without considering which it is impossible to describe quantitatively the properties of a polymeric substance.⁴ Examples of the simplest UOD are illustrated in Fig. 1.

There have been numerous studies devoted to the role of entanglements of the macromolecules in the dynamics of melts

and concentrated polymer solutions.^{5–8} The level of disorder must influence the mechanical properties of the polymeric substance, which depend on the nature of the entanglements of the macromolecules.⁹ However, consideration of these questions is outside the scope of the present review, in which attention is concentrated on the relation between the topological disorder and the physicochemical properties of the polymer–low-molecular substance system.

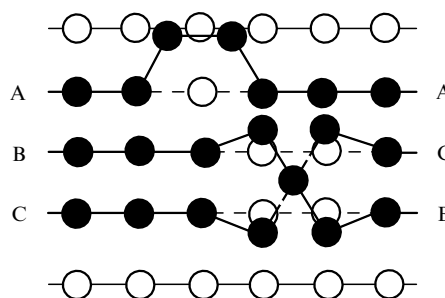


Figure 1. Schematic illustration of the simplest unit of disorder: A—A—fold; B—B and C—C—entanglement.

II. The homopolymer as a two-component system

There exists an extensive class of crystallising polymers, such as polyethylene, polypropylene, poly(vinyl chloride), aliphatic polyamides, *etc.* A characteristic feature of these polymers is incomplete crystallisation. The physical cause preventing the complete crystallisation of the polymeric substance is the presence of a stable disorder in the arrangement of the polymer chains. The ‘crystallinity’, *i.e.* the content of the crystalline substance in such polymers, varies as a rule within wide limits (from 20% to 80%)¹⁰ and may change reversibly with temperature¹¹ and apparently with pressure. It is noteworthy that the absolute value of the ‘crystallinity’ of the same polymer measured in different ways can differ appreciably, so that in speaking of the ‘crystallinity’ of the

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polymer it is always necessary to indicate the method used for its measurement.¹²

Incomplete crystallisation implies that two phases coexist in the individual homopolymer over a certain range of temperatures and pressures: crystalline and amorphous. According to Gibbs' phase rule

$$F + P \leq C + 2, \quad (1)$$

where $F = 2$ is the number of degrees of freedom (temperature and pressure), $P = 2$ is the number of phases (crystalline and amorphous), and C is the number of components which should be at least two. If the disorder units (or the units of disorder) are adopted as the quasi-molecules of a second component, then the degree of disorder can be expressed in concentration units. Taking into account the wide variety of the disorder elements ζ_i , one can write

$$[\zeta] = \sum [\zeta_i] = \frac{1}{VN_A} \sum N_i, \quad (2)$$

where V is the volume of the sample, N_A is the Avogadro number, and N_i is the number of UOD of the i th type in the sample.

Like the species of a low-molecular substance, the quasi-molecules can migrate, although to a limited extent, in the polymer melt; the folds (A–A in Fig. 1) migrate *via* a wavelike motion ('reptation'?), whilst the simplest knots (B–B and C–C) migrate *via* a mechanism in which the monomer units adjoining the knot change places ('sliding' along parallel chains).

Assuming that the complete crystallisation of the polymer is prevented by the osmotic pressure of the solution of the UOD in the noncrystallised part of the polymer, which is $P_{os} = RT[\zeta](1-x)^{-1}$ (x is the degree of crystallinity), the author of the present review² proposed an equation describing the dependence of the degree of crystallinity of the polymer on the concentration of extraneous units ω_i

$$(1-x) = \frac{RT[\zeta]}{-\Delta F_{cr} - \sum_i \kappa_i [\omega_i]}, \quad (3)$$

where $-\Delta F_{cr}$ is the decrease in free energy on crystallisation of the polymer calculated per unit mass of the latter and κ_i are coefficients taking into account the decrease in $-\Delta F_{cr}$ when foreign units of the i th type are incorporated in the crystallite. As can be seen from Eqn (3), for $[\zeta] = 0$ the polymer crystallises fully (*i.e.* $x = 1$) and conversely, above a certain value of $[\zeta]$, the polymer is fully amorphous.

III. Methods for the investigation of the degree of disorder

Any violation of short-range order is associated with a certain excess volume: the density of the polymeric substance in the region of the entanglement of the polymer chains should be reduced. Thus the UOD, or more precisely the structural formations Z_j arising from them, may be regarded as elements of the free volume. Just as one can measure the volume of a vessel by filling it with water or another liquid, the free volume corresponding to the structural formation Z_j is measured by filling it with a low-molecular substance. However, owing to the smallness of the volume of the element Z_j , only those substances the molecular volume of which V_A is not greater than the free volume V_j contained in this element can fill it (or, more precisely, be placed in it):

$$V_A \leq \beta V_j, \quad (4)$$

where β is the coefficient taking into account the lack of correspondence between the shapes of the molecule of substance A and the volume element ζ_j . Thus, by investigating the dissolution (sorption) of various low-molecular substances in the polymer, it is possible to obtain information about the concentration of the UOD and their size distribution for the dissolved (sorbed) molecules.

The density of the polymer or, more precisely, the difference between the theoretical calculated volume of unit mass of the ideally crystallised polymer and the real volume of unit mass of the sample studied (the so-called free volume) might serve as a natural measure of the free volume, but in such an approach we cannot estimate the size distribution of the elements of the free volume. Furthermore, the most sensitive method for the determination of density — hydrostatic weighing — requires the immersion of the sample in a low-molecular liquid the molecules of which partly fill these elements.

Assuming that the sorption of substance A includes a stage involving the formation of a true solution of A in the amorphous part of the polymer with its subsequent permeation into the sorption centres in accordance with the scheme



and that the first stage obeys Henry's law

$$[A] = \gamma_A [A]_m, \quad (6)$$

where $[A]$ is the concentration of truly dissolved molecules of A, $[A]_m$ is the concentration of A in the surrounding medium, and γ_A is Henry's coefficient, it is easy to find the isotherm for the sorption of substance A by the polymer from the formula

$$[A]_p = \gamma_A [A]_m + \sum_j [AZ_j] = \gamma_A [A]_m + \sum_j \frac{\gamma_A K_j [Z_j] [A]_m}{1 + \gamma_A K_j [A]_m} \quad (7)$$

or, neglecting the true solubility of A outside the sorption centres, from the formula

$$[A]_p = \sum_j \frac{\gamma_A K_j [Z_j] [A]_m}{1 + \gamma_A K_j [A]_m}. \quad (8)$$

With increase in the concentration of the molecules of A in the surrounding medium, each term in Eqn (8) tends to $[Z_j]$ and $[A]_p$ tends to $\sum [Z_j] = [Z_A]$ (the overall concentration of the centres sorbing the given substance).

It will be shown below that, even for considerable differences between the sorption constants K_j , the isotherm for sorption on inhomogeneous centres is experimentally indistinguishable from the Langmuir isotherm

$$[A]_p = \frac{a[A]_m}{1 + b[A]_m}. \quad (9)$$

However, for high values of $[A]_m$, this relation may break down. Remaining in the region where the Langmuir Law holds, it is possible to determine the 'Langmuir sorption capacity',^{13,14} *i.e.* the value $[Z_A]$. The type (9) Langmuir relation can be transformed into a straight line in terms of the variables $1/[A]_m$ and $1/[A]_p$, whereupon the intercept made by the straight line on the ordinate axis corresponds to the reciprocal of the concentration of the sorption centres: $b/a = 1/[Z_A]$.

On the simplest assumption that within a certain range $K_1 \leq K_i \leq K_2$ the value of

$$\rho = \frac{\Delta[Z_i]}{\Delta K_i} = \frac{[Z_A]}{K_2 - K_1} \quad (10)$$

is constant and that outside this range it is zero, we arrive at the following expression after substituting the sum (8) by the integral:

$$[A]_p = \rho \int_{K_1}^{K_2} \frac{K \gamma_A [A]_m dK}{1 + K \gamma_A [A]_m} = [Z_A] \left\{ 1 + \frac{1}{(K_2 - K_1) \gamma_A [A]_m} \ln \frac{1 + K_1 \gamma_A [A]_m}{1 + K_2 \gamma_A [A]_m} \right\}. \quad (11)$$

When $[A]_m \rightarrow \infty$, the value $[A]_p$ tends to the limit $\lim [A]_p = [Z_A]$.

Figure 2 presents the curve for the dependence of $[A]_p$, or, more precisely, of the ratio $[A]_p/[Z_A]$, on $[A]_m$, calculated by

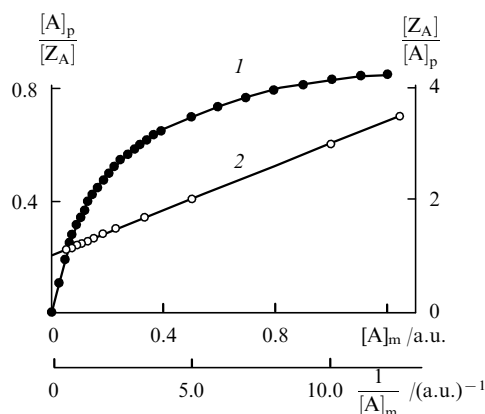


Figure 2. The sorption isotherm of a low-molecular substance by a polymer in direct (1) and inverse (2) coordinates: calculation by Eqn (11) with $K_2/K_1 = 10$.

Eqn (11) with $\gamma_A = 1$, $K = 1$, and $K_2 = 10$ in terms of the direct variables and their reciprocals. It is seen from the figure that the curve described by Eqn (11) in inverse coordinates $1/[A]_p$ vs. $1/[A]_m$ is transformed into a straight line, which means that Eqn (11) may be replaced by the simpler expression

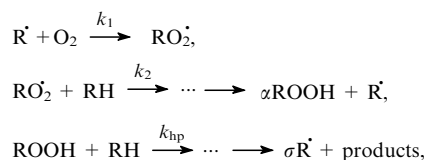
$$[A]_p = \frac{[Z_A] K \gamma_A [A]_m}{1 + K \gamma_A [A]_m}.$$

Apparently the majority of the phenomena associated with the role of disorder may be satisfactorily explained by assuming that the UOD can be divided, for any influence, into those participating or not participating in the process and those which respond in different ways to the given influence (in all cases, the quantitative differences within each group are neglected).

In certain cases, it is possible to employ the equilibrium solubility of substance A in the polymer (S_A) as a measure of the concentration of the centres $[Z_A]$. Evidently the value S_A is always smaller than $[Z_A]$, but in some instances, when S_A is close to its theoretical limit $[Z_A]$, one can assume that $S_A \approx [Z_A]$. The closeness of S_A to $[Z_A]$ may be indicated, for example, by a weak temperature dependence of the solubility.

If the substance dissolved in the polymer is an antioxidant, it is possible to estimate the change in the concentration of its mobile part by the method of critical concentrations. This method has been described in detail^{15,16} and here we shall consider only its simplified version.

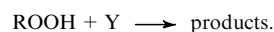
In order to inhibit a radical chain oxidation reaction occurring in a polymer consisting of RH units, *i.e.*



where R' is a free radical (usually a hydrocarbon), ROOH is the branching product reacting with the initial substance to form new free radicals, α is the yield of hydroperoxy-groups, and σ is the probability of degenerate chain branching, it is necessary to introduce into the reacting substance an inhibitor IH.¹⁷



or a substance Y which reacts with the branching product, *i.e.*



In the former case, the balance of the RO_2' and ROOH concentrations is described by the system of equations

$$\frac{d[RO_2']}{dt} = W_0 + \sigma k_{hp}[ROOH][RH] - k_t[RO_2'][IH], \quad (13)$$

$$\frac{d[ROOH]}{dt} = \alpha k_2[RO_2'][RH] - k_{hp}[ROOH][RH]. \quad (14)$$

Here W_0 is the rate of chain initiation.

Assuming that the RO_2' concentration is stationary, *i.e.* that the rates of formation and consumption of RO_2' are equal, $d[RO_2']/dt = 0$, one can write

$$[RO_2'] = \frac{W_0 + \sigma k_{hp}[ROOH][RH]}{k_t[IH]}.$$

Neglecting the rate of chain initiation W_0 compared with the rate of branching $\sigma k_{hp}[ROOH]$, we find

$$\frac{d[ROOH]}{dt} = \frac{k_{hp}[ROOH][RH]}{k_t[IH]} (\alpha \sigma k_2[RH] - k_t[IH]). \quad (15)$$

As can be seen from the last expression, the value of $d[ROOH]/dt$ is positive, *i.e.* the process is self-accelerated, provided that the expression in brackets is positive, *i.e.*

$$(\alpha \sigma k_2[RH] - k_t[IH]) > 0 \quad (16)$$

or

$$[IH] < [IH]_{cr} = \frac{\alpha \sigma k_2[RH]}{k_t} \quad (17)$$

and, conversely, the rate of the process decreases, tending to a limit, if this expression is less than zero.

The quantity $[IH]_{cr}$, *i.e.* the concentration of the inhibitor (antioxidant) corresponding to the boundary between the two reaction regimes, is called the critical concentration. Compounds which decompose the branching product may displace the critical concentration of the inhibitor but they themselves do not have a critical concentration in the absence of an inhibitor.^{16,17}

The critical concentration of the antioxidant can be determined experimentally comparatively easily as the boundary between the region of the relatively slow stationary process and the fast self-accelerated process.¹⁸ In particular, the induction period, *i.e.* the period during which the fast reaction is suppressed by the antioxidant, does not increase or increases slowly for $[IH] < [IH]_{cr}$ and rapidly for $[IH] > [IH]_{cr}$, which is manifested as a break in the curve for the dependence of the induction period on the initial antioxidant concentration for $[IH]_0 = [IH]_{cr}$.^{16,18}

The antioxidant molecules are divided into those bound into the complexes $Z_i IH$ with the sorption centres and the mobile molecules IH. Mainly the mobile molecules IH participate in the chain termination in the solution in the polymer with participation of the macroradicals M' and MO_2' , the translational mobility of which is close to zero. The concentration of mobile molecules is related to the overall IH concentration in the polymer by the expression

$$[IH] = \frac{[IH]_p}{K_{IH}[Z_{IH}]} \quad (18)$$

where $[Z_{IH}]$ is the concentration of the IH-sorbing centres and K_{IH} is the sorption equilibrium constant; the equation is valid only at low antioxidant concentrations $[IH] \ll [Z_{IH}]$, such as the critical concentrations. Thus the difference between the experimental critical concentrations of the same antioxidant in different samples of a polymer of the same chemical nature is determined by the difference between the concentrations and properties of the sorption centres, *i.e.* the difference in the character of the disorder in the arrangement of the polymer chains. The method of critical concentrations can be used in those cases where the method for the investigation of the sorption isotherm is for one or another reason inapplicable, in particular in the study of polymer melts.

IV. Sorption of low-molecular substances by the polymer

We shall examine the equilibrium sorption of a low-molecular substance — phenyl benzoate (A) — by polyethylene as the simplest example. The curves for the dependence of the concentration of this substance in polyethylene $[A]_p$ on its concentration in the gas phase $[A]_m$ surrounding the polymer are transformed into straight lines when $1/[A]_p$ is plotted against $1/[A]_m$ (Fig. 3)¹⁹ and all the straight lines corresponding to temperatures ranging from 80 to 180 °C, *i.e.* from the solid polymer to its melt, intersect the ordinate axis at the same point corresponding to $[Z_A] = 0.55 \text{ mol kg}^{-1}$. The experimentally observed linear relations of the type

$$\frac{1}{[A]_p} = \frac{1}{[Z_A]} + \frac{K_A \gamma_A [Z_A]}{[A]_m} \quad (19)$$

may be transformed into relations of the 'Langmuir' type

$$[A]_p = \frac{K_A \gamma_A [Z_A] [A]_m}{1 + K_A \gamma_A [A]_m} \quad (20)$$

with $[Z_A] = \text{const.}$

The temperature independence of $[Z_A]$ and the fact that it does not change even on passing through the melting region ($\sim 130^\circ\text{C}$ for polyethylene) agree well with the topological nature of the sorption centres: the folds, knots, and entanglements of the long polymer chains do not disappear on melting the polymer. Many other substances behave similarly to phenyl benzoate on sorption from both the gas phase and from solutions in low-molecular liquids (Fig. 4).²⁰ The limit of the sorption from solutions, *i.e.* the value $[Z_A]$, is as a rule lower than in sorption from the gas phase and depends on the nature of the solvent.²¹ In more complex cases at simultaneous sorption of two different substances from the same solvent, one substance is displaced from solution in the polymer by the other.

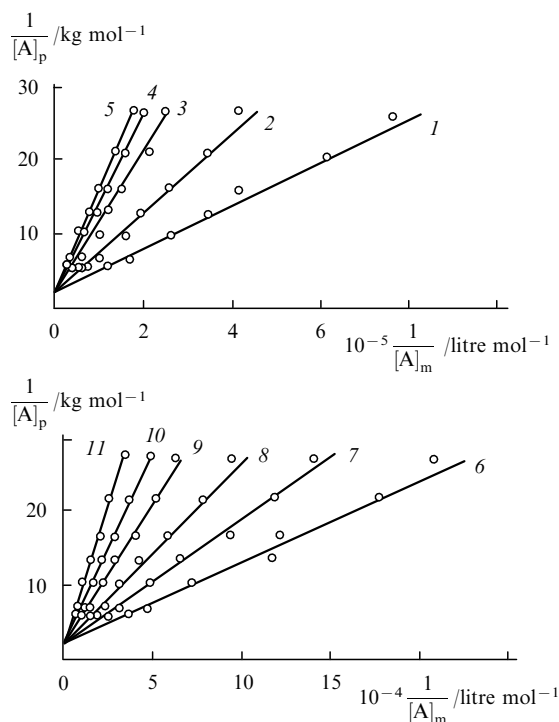


Figure 3. The sorption isotherm of phenyl benzoate by high-density polyethylene from the gas phase.¹⁹ Temperature (°C): (1) 80; (2) 90; (3) 100; (4) 110; (5) 120; (6) 130; (7) 140; (8) 150; (9) 160; (10) 170; (11) 180.

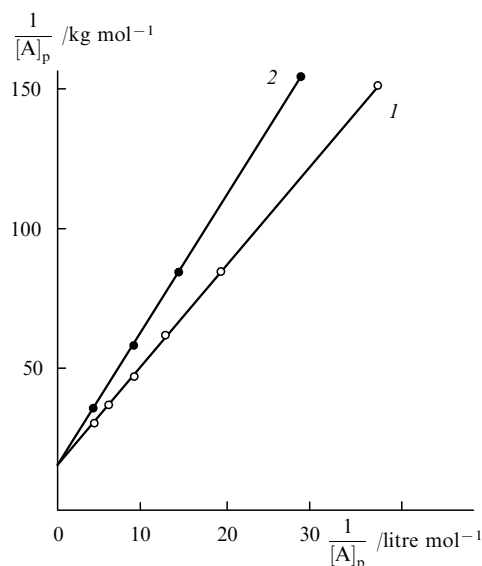


Figure 4. The sorption isotherm of phenyl benzoate (1) and diphenylamine (2) by high-density polyethylene from n-hexane at 50 °C in the coordinates $1/[A]_p - 1/[A]_m$.²⁰

Suppose that two substances, A and B, are sorbed by the same centres Z_i . One may then expect that these substances will compete for the sorption centres, *i.e.* the process



will take place. As a result, the solubility of substance A in the polymer will decrease with increase in the concentration of substance B in the surrounding medium. Such a relation has been frequently observed in practice (Fig. 5).^{20, 22}

However, in certain cases a more complex relation holds: maxima appear on the descending curve for the dependence of the solubility of one substance on the concentration of the other (Fig. 6).²⁰ These maxima can be explained by the formation of more complicated complexes ABZ_j on certain sorption centres Z_j .



The solvent can also function as the second substance, which results in a change of the nature of the sorption isotherm. This explains the dependence of the solubility of low-molecular substances on the nature of the solvent from which the given substance is sorbed, which has been observed in a number of experiments.²¹

The sorption centres may be various microcavities the formation of which is not connected directly to the disorder in the

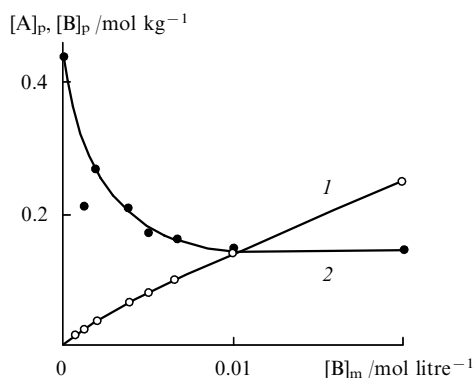


Figure 5. Dependence of the concentrations of α -naphthol (A) (1) and α -naphthylamine (B) (2) in high-density polyethylene on the α -naphthylamine concentration in hexane at 50 °C.²⁰

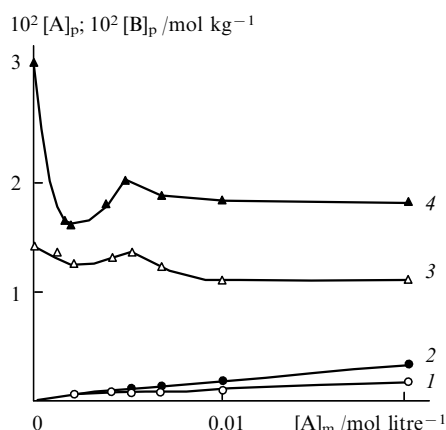


Figure 6. Dependence of the equilibrium concentrations of α -naphthol $[A]_p$ (1, 2) and diphenylmethane $[B]_p$ (3, 4) in high-density polyethylene (1, 3) and low-density polyethylene (2, 4) on the α -naphthol concentration in isopropyl alcohol at 50 °C {diphenylmethane concentration in solution $[B]_m = 0.2 \text{ M}$ }.²⁰

arrangement of the polymer chains and which vanish when the samples are pressed under high pressure.²³

The sorption is related directly to the diffusion of the dissolved substance. Assuming that only the mobile molecules of A outside these centres participate in the diffusion, it is possible to find the theoretical dependence of the (observed) diffusion coefficient on the overall concentration of substance A in the polymer. According to Fick's first law, the flow of molecules of A through a unit cross-section of the polymer sample, perpendicular to the x axis, is

$$\Phi = -D_r \frac{d[A]}{dx} = -D_r \frac{d[A]}{d[A]_p} \frac{d[A]_p}{dx} = -D_{\text{eff}} \frac{d[A]_p}{dx}, \quad (23)$$

where D_r and D_{eff} are the true and observed diffusion coefficients.

The observed diffusion coefficient of substance A in the polymer is given by $D_{\text{eff}} = D_r \{d[A]/d[A]_p\}$. For low values of $[A]_p$ ($[A]_p < [Z_A]$), we have $[A] = [A]_p / K_A \{ [Z_A] - [A]_p \}$. On differentiating this value with respect to $[A]_p$, we obtain²⁴

$$D_{\text{eff}} = \frac{D_r [Z_A]}{K_A ([Z_A] - [A]_p)^2}. \quad (24)$$

A similar formula has been derived by Fujita.²⁵ In a study²⁶ of the diffusion of 2,2'-methylenebis(6-*tert*-butyl-4-methylphenol), labelled with ^{14}C , into polyethylene containing the same but not radioactive substance at different concentrations, not only was Eqn (24) confirmed but a value of $[Z_A]$ virtually identical with the solubility ($0.034 \text{ mol kg}^{-1}$ at 80 °C) was calculated.

It was later shown with the aid of the NMR method²⁷ that the molecules of ammonia dissolved in polystyrene can be divided into highly and weakly mobile, their mobilities differing by a factor of 20.

V. Formation of sorption centres in the sedimentation of polymers from solution

We shall consider the case where the polymer is formed in sedimentation from solution in a low-molecular liquid.²⁸ Evidently, the sedimentation must be preceded by the sticking together of sections of the polymer chains and the elements of future disturbed-order knots ζ_i^* are then laid down in the polymer.

Suppose that the element ζ_i^* contains a certain volume of the solvent v_i^* . Assuming that the energy of formation of this volume is proportional to the latter and to the difference between the energies of the interaction of the monomer unit of the polymer with another such unit and with the solvent ($q_p - q_s$), i.e.

$\varepsilon_i = v_i^*(q_p - q_s)$, we find that the probability of the formation of the volume element $v_i^* \geq v_A^*$ is

$$p_A = C \exp\left(\frac{-\varepsilon_A}{kT}\right) = C \exp\left[\frac{-v_A^*(q_p - q_s)}{kT}\right]. \quad (25)$$

On sedimentation of the polymer, the structures ζ_i^* are deformed. It is natural to postulate that the greater the volume v_i^* of the element ζ_i^* present in the solution the greater the volume v_i^* of the element ζ_i^* produced from it in the polymeric substance formed. After introducing the proportionality coefficient β , we find an expression for the concentration of the centres $[Z_A]$ in the deposited polymer:

$$[Z_A] = [Z]_0 \exp\left[\frac{-v_A^* \beta (q_p - q_s)}{kT}\right]. \quad (26)$$

The value $[Z_A]$ in Eqn (26) is equal to the concentration of the UOD around which the elements of the free volume may be formed. If it is assumed that such centres are produced around the point of contact between two sections of the same or different polymer chains, then the concentration of these elements is higher, the higher the concentration of the polymer in solution at the instant of sedimentation.

Eqn (26) describes the law of the distribution of the sorption centres with respect to the volume of the molecules sorbed by them. In the sorption of organic substances consisting of C, H, O, and N atoms, the densities of which in the pure state differ little ($\rho_A = 1.1 \pm 0.1 \text{ g cm}^{-3}$), one can assume that $v_A = M_A(\rho_A N_A)^{-1}$, where $N_A = 6.02 \times 10^{23}$ is the Avogadro number. In this case, Eqn (26) transforms into

$$[Z_A] = [Z]_0 \exp(-\kappa M), \quad (27)$$

where

$$\kappa = \frac{\beta(q_p - q_s)}{\rho N_A k T_s}. \quad (28)$$

Here T_s denotes the temperature of the formation of the centre, i.e. the temperature of the sedimentation of the polymer from solution.

As can be seen from Fig. 7,^{28,29} Eqn (28) agrees well with experimental data and the value $q_p - q_s$ found from the slope of the straight line proved to be 51 J cm^{-3} . For comparison, we may note that the heat of melting of polyethylene crystals is 293 J g^{-1} .

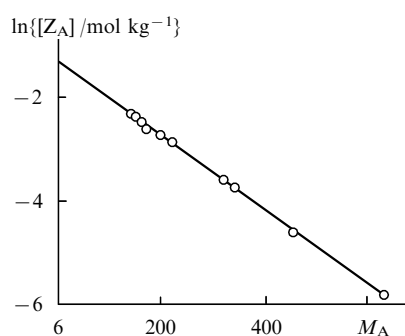


Figure 7. Dependence of the logarithm of the concentration of the sorption centres for low-molecular substances $\ln[Z_A]$ in high-density polyethylene on the molecular mass of the sorbed substance (M_A) at 50 °C (solvent — n-hexane).²⁹

VI. Rearrangement of the sorption centres under the influence of the dissolved substance

As shown above (Fig. 3), the Langmuir sorption limit, i.e. the value $[Z_A]$, in most cases remains constant over a wide range of temperatures (from the temperature of the existence of the solid polymer to the melting point). However, when an additive is

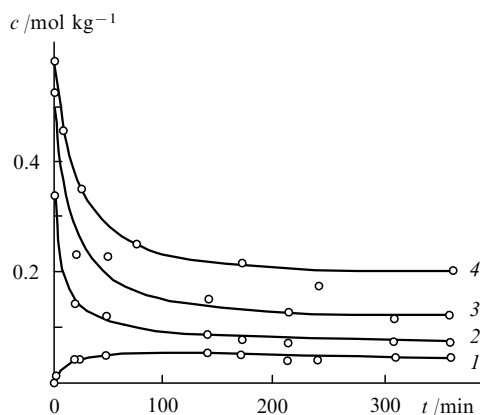


Figure 8. Variation of the concentration of phenyl benzoate in isotactic polypropylene in the saturated vapour of this compound at 40 °C. Initial phenyl benzoate concentration in the melt (240 °C) (mol kg⁻¹) (1) 0; (2) 0.34; (3) 0.53; (4) 0.58.³³

introduced directly into the melt, the sorption law may be infringed.^{30–33} The sorption limit may then increase significantly.

Figure 8 illustrates the variation of the concentration of phenyl benzoate, introduced into a melt of isotactic polypropylene at different initial concentrations, when cooled polymer samples are kept in sealed tubes containing an excess of phenyl benzoate. In the course of such experiments, a large proportion of the dissolved substance escapes from the polymer, but its residual concentration exceeds appreciably the solubility in the untreated polymer. If a low-molecular substance A is introduced into the polymer melt at a concentration exceeding the solubility $\{[A]_p > [Z_A]\}$ and the substance is then extracted from the melt with alcohol at a low temperature (40 °C), then its solubility in the treated polymer is found to be appreciably higher than in the untreated polymer.³⁰ When such samples are heated to 80–100 °C, the solubility gradually falls to the initial value. These processes may be represented schematically as follows:



where ζ_k are the elements of disorder, which do not give rise to sorption centres under normal conditions, while Z_k are sorption centres formed around these elements at high concentrations of substance A.

The rearrangement of the elements ζ_k to sorption centres is accompanied by an increase in the free volume contained in them, which requires the consumption of the energy $\Delta\epsilon_k = (q_p - q_A)\Delta v_k$ where q_A is the energy of the interaction of the element of the polymer chain with the additive A referred to unit volume. The dimensions of the values q_p , q_s , and q_A (energy/volume) are identical with the dimension of pressure and in terms of its physical significance q is equal to the osmotic pressure of substance A in the polymer required for the rearrangement of the centres (*i.e.* for the 'fracture' of the polymer structure):

$$RT[A] \approx \frac{RT[A_p]}{[Z_A]K_A},$$

where $[A]$ is the concentration of mobile molecules, while $[A]_p$ is the overall concentration of substance A in the polymer. Since the parameters of the initial elements ζ_k do not enter into the expression for $\Delta\epsilon_k$, this pressure must be identical for all the elements and the rearrangement of all the centres must begin at the same concentration of the given additive. As can be seen from Fig. 9, the solubilities (L) of phenyl- β -naphthylamine and phenyl benzoate in polypropylene begin to increase at the following concentrations of these additives in the melt; ~ 0.15 and 0.25 mol kg⁻¹ respectively.

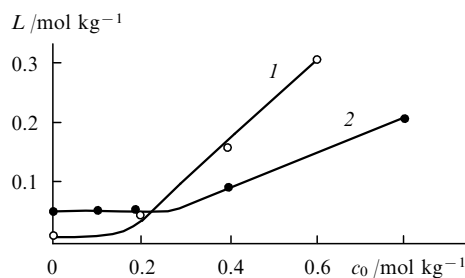


Figure 9. The solubilities (L) of phenyl- β -naphthylamine (1) and phenyl benzoate (2) in isotactic polypropylene at 40 °C as a function of the initial concentration of the same substance in the melt (240 °C).³⁴

VII. The possibility of varying the degree of disorder on reprecipitation of the polymer

According to Eqns (26) and (27),²⁸ the level of topological disorder, *i.e.* the overall concentration of the elements ζ_i and their size distribution, depend on the conditions governing the formation of the polymeric substance during its sedimentation from solution — on the nature of the solvent, the concentration, and temperature, *i.e.* on the value q_A . All these methods for the variation of the level of disorder have been used in our studies.

It is natural to postulate that the smallest values of q_A will be observed on precipitation of nonpolar polyalkenes from their low-molecular analogues — saturated hydrocarbons, and the highest will be observed on sedimentation from polar aromatic compounds. Indeed, the samples obtained by the reprecipitation of isotactic polypropylene from solutions in *n*-decane and chlorobenzene (5 g per 150 ml) differed appreciably in their properties. The crystallinities of polypropylene reprecipitated from *n*-decane and chlorobenzene, determined by differential scanning calorimetry, were 61.2% and 69.2%, and their densities were 0.9115 and 0.9179 g cm⁻³ respectively. The equilibrium solubilities of antioxidants in the samples of isotactic polypropylene precipitated from solutions in *n*-decane and chlorobenzene at 60 °C were 0.02 and 0.01 mol kg⁻¹ for phenyl- β -naphthylamine and 0.17 and 0.13 mol kg⁻¹ for phenyl benzoate which has the lower molecular weight. The sorption isotherms of phenyl- β -naphthylamine from alcohol by these samples (Fig. 10) differed even more³⁴ while the values of $[Z]_A$ calculated from them differed by a factor of 7.7 (0.30 and 0.039 mol kg⁻¹). It must be emphasised that the powders obtained on reprecipitation of polypropylene were pressed into films at temperatures in the range 200–220 °C, *i.e.* above the melting points of both samples (158.5 and 160.1 °C respectively).

The inhibited oxidation of the polymer samples was investigated at 180 °C, *i.e.* above the melting point. The experiments showed that the critical concentrations of the antioxidant (phenyl-

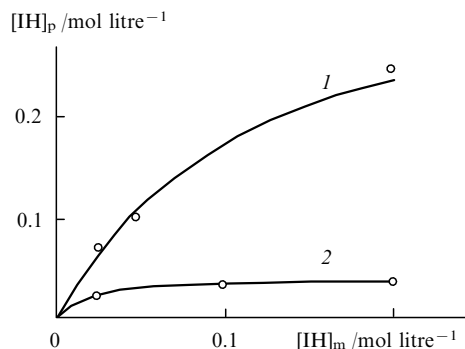


Figure 10. The sorption isotherms of phenyl- β -naphthylamine by samples of polypropylene reprecipitated from *n*-decane (1) and chlorobenzene (2) (solvent — alcohol, temperature — 40 °C).³⁴

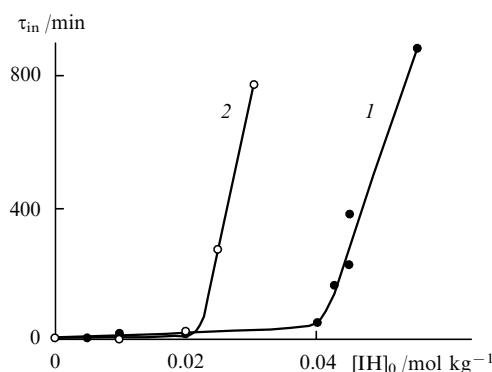


Figure 11. Dependence of the induction period in the oxidation of polypropylene samples on the initial concentration of phenyl- β -naphthylamine (180 °C, oxygen, 300 mmHg): (1) polymer reprecipitated from *n*-decane; (2) polymer reprecipitated from chlorobenzene.³⁰

β -naphthylamine) in these samples differed by a factor of 1.9 (Fig. 11), the higher value corresponding to samples reprecipitated from *n*-decane.³⁴ Thus the difference between the concentrations of the sorption centres arising on reprecipitation of the polymer is preserved also in the melt.

Eqn (28) contains the temperature of the polymer sedimentation T_s . In the study of Kolesnikova and Shlyapnikov,³⁵ a solution of polypropylene in *m*-xylene at a temperature of 130 °C was either mixed with cold alcohol (rapid cooling) or was slowly cooled to room temperature. In the former case, the centres existing at 130 °C (isothermal conditions) were rapidly frozen, while in the latter the sedimentation occurred under nonisothermal conditions (~ 80 °C). The polypropylene samples obtained differed both in the sorption isotherms of phenyl- β -naphthylamine from ethyl alcohol and in the critical concentrations of the phenyl- β -naphthylamine used as the antioxidant in the oxidation of their melts; the latter are $0.055 \text{ mol kg}^{-1}$ (in the samples prepared by rapid cooling) and $0.040 \text{ mol kg}^{-1}$ (in the samples prepared by the slow cooling of the solution).

In the study of Mar'in *et al.*,³⁶ samples of isotactic polypropylene were subjected to a treatment involving repeated 'melting–crystallisation' cycles in accordance with the following scheme: heating to 250 °C, maintenance at this temperature for 90 min, cooling to 150 °C for 120 min, maintenance at this temperature for 120 min, and then cooling to room temperature. It was postulated that, by displacing segments of the macromolecules, the growing crystal facets can 'disentangle' some of their knots. The solubilities of diphenylamine, phenyl benzoate, and phenyl- β -naphthylamine but not the sorption isotherms were used as a measure of disorder. It can be seen from Table 1³⁶ that, as a result of seven cycles, the solubility of diphenylamine (molecular mass $M = 169$) decreased 3.7 fold, that of phenyl benzoate ($M = 199$) fell by a factor of 1.6, while that of phenyl- β -naphthylamine ($M = 219$) decreased by only 15%. Thus the larger the molecule, the greater the volume of its sorption centre and hence the more complex the UOD constituting its basis and the greater its resistance to disentanglement.

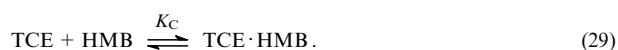
Table 1. Variation of the solubilities of low-molecular probe substances as a function of the number of melting–crystallisation cycles of isotactic polypropylene (according to the data of Shlyapnikov and coworkers^{19,36}).

Substance	Molecular mass	Number of cycles			
		1	3	5	7
Diphenylamine	169	0.234	0.208	0.068	0.063
Phenyl benzoate	199	0.162	0.142	0.130	0.102
Phenyl- β -naphthylamine	219	0.0148	0.0138	0.0135	0.0128

VIII. The anomalies in certain equilibria

It follows from Eqn (27) that the value of $[Z]_0$ depends on the concentration of the polymer solution from which the sample has been prepared by precipitation.

The formation of a complex between tetracyanoethylene (TCE) and hexamethylbenzene (HMB) in polyethylene and polypropylene has been investigated.³⁷



In our study of complex formation in the polymer, we were forced to compare the overall concentrations of the individual substances and complexes, *i.e.* to assume that $[\text{TCE}]_p \approx [\text{TCE} \cdot \text{Z}_{\text{TCE}}]$, *etc.*, whereas in fact a series of equilibria of type (21) occur in the polymer. According to Eqn (26), the concentrations of sorption centres decrease rapidly with increase in the molecular mass of the sorbed substance. Since the concentration of the complex under the comparatively mild conditions used in the study of the reaction (20–60 °C) cannot be higher than the concentration of the centres sorbing these complexes, a dependence of the concentration of the complexes, and of the complex formation constant K_c calculated from it, on the concentration of the solution of polyethylene in *n*-decane at the instant of its sedimentation was observed in the experiments (Fig. 12).

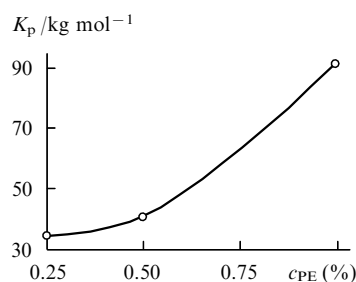


Figure 12. Dependence of the apparent equilibrium constant (measured at 22 °C) for the formation of a complex between hexamethylbenzene and tetracyanoethene in polyethylene on the concentration of polyethylene at the instant of its sedimentation in *n*-decane at 120 °C.³⁸

IX. Characteristic features of the kinetics of chemical reactions in polymers

Three types of relatively simple nonchain reactions occurring in polymers have been studied in detail.



Deviations from the regular features of the analogous reactions in the liquid phase were discovered.

A reaction of the first type may take place *via* two mechanisms: within and outside the centres Z_A and the centres can in their turn differ in their sorption energy. In order to simplify the calculations, we shall assume that all the centres are identical and that the reaction can proceed either within the centres or outside them. Denoting the rate constant for the reaction within the centres by k_{AZ} and that outside the centres by k_A , we find the expression for the overall rate of reaction;

$$-\frac{d[\text{A}]_p}{dt} = k_A[\text{A}] + k_{AZ}([\text{A}]_p - [\text{A}]). \quad (33)$$

Since a large proportion of the dissolved substance is usually contained within the sorption centres, *i.e.* $[A] \ll [A]_p$, appreciable deviations of the reactions from first order are observed only in the case where $k_A \gg k_{AZ}$. If compound A decomposes *via* the intermediate reversible formation of a radical pair,



then the volume required for the formation of the pair will be always greater than the volume of the initial molecule and the formation of a 'cage', coinciding with the sorption centre, will require an additional energy. For this reason, the rate of reaction within the centre should be appreciably lower than outside it. In the centres the shape of which corresponds most closely to that of the molecules contained in them, any reactions proceeding with a change in the shape of the reacting molecule will be hindered.

On the basis of general considerations, one may expect that the condition $k_A \gg k_{AZ}$ is obeyed and that the apparent rate constant (the ratio of the rate to the product of the concentrations of the reactants) increases with increase in the initial concentration of the reactant. Indeed, such a relation has been observed in the thermal decomposition of benzoyl peroxide $C_6H_5C(O)-O-O-C(O)C_6H_5$ in isotactic polypropylene (Fig. 13).³⁸ The reaction was catalysed by adding phenyl benzoate, which could substitute the peroxide molecules in the sorption centres. Similarly, the rate of isomerisation of dimethylbenzylsilyl peroxide in the same polymer increased with increase in its concentration.³⁹ It has been shown⁴⁰ that the total yield of the free radicals formed on decomposition of azobisisobutyronitrile in isotactic polypropylene at 80 °C increases nonlinearly with increase in the concentration of this substance: from 0.12 (at an initial concentration of 0.075 mol kg⁻¹) to 0.40 (at a concentration of 0.025 mol kg⁻¹).

Reactions of the second type have been investigated in detail in the interaction of benzoyl peroxide and diphenylethyl hydroperoxide with dibenzyl sulfide⁴¹⁻⁴³ and of benzoyl peroxide with

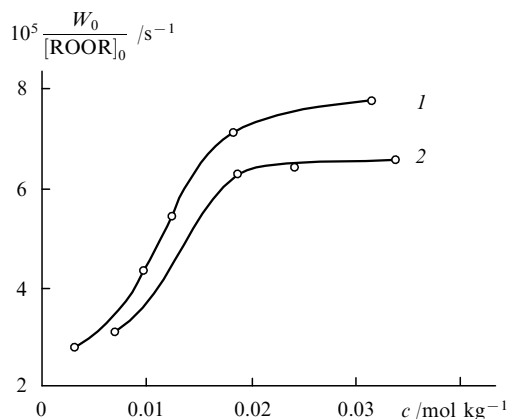


Figure 13. Dependence of the effective rate constant of the thermal decomposition of benzoyl peroxide (80 °C) in isotactic polypropylene on the initial peroxide concentration: (1) usual polymer; (2) polymer with an increased concentration of sorption centres.³⁸

diphenylamine.⁴⁴ These reactions can proceed *via* several paths:



If the concentrations of the free molecules of A and B are low compared with those of the bound molecules, the first path appears improbable and we shall therefore consider only the three remaining ones.

It was shown above that, despite the diversity of the sorption centres, the sorption isotherms of the individual substances are described satisfactorily by Langmuir isotherms in which K_A and K_B are average values and $[Z_A]$ and $[Z_B]$ are the total concentrations of the centres sorbing the given substance.

On solving the equation $[AZ_A] = K_A[Z_A][A]\{1 + K_A[A]\}^{-1}$ for $[A]$ and substituting $[AZ_A] + [A] = [A]_p$, we obtain a fairly cumbersome expression:⁴⁴

$$[A] = \frac{K_A[A]_p - K_A[Z_A] - 1}{2K_A} + \frac{\sqrt{(1 + K_A[Z_A] - K_A[A]_p)^2 + 4K_A[A]_p}}{2K_A}. \quad (38)$$

The dependence of $[A]/[A]_p$ (the fraction of mobile molecules) on $[A]_p/[Z_A]$ calculated by this formula is presented in Fig. 14 for different values of K_A . As can be seen from the figure, the fraction of mobile molecules increases with increase in the overall concentration of the reactant $[A]_p$, the increase being especially rapid starting from $[A]_p/[Z_A] = 1$.

The concentration of the complexes ABZ_{AB} varies with increase in the concentrations of the reactants in accordance with the equation^{41, 42}

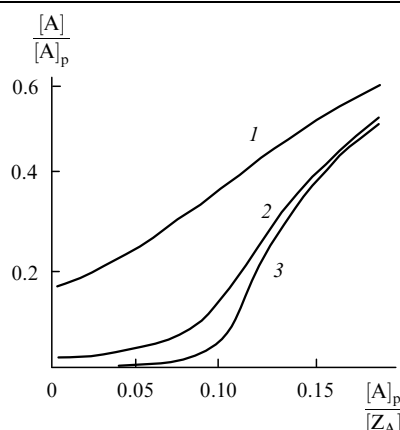


Figure 14. Dependence of the fraction of mobile molecules {of the ratio $[A]/[A]_p$ } on the overall concentration of substance A in the polymer {in units of $[A]_p/[Z_A]$ } [calculation by Eqn (38)].^{41, 43}

$$[ABZ_{AB}] = \frac{K_{AB}[Z_{AB}][A][B]}{1 + K_{AB}[A][B]}. \quad (39)$$

At low concentrations of A and B $\{[A]_p \ll [Z_A]; [B]_p \gg [Z_B]\}$, one may put $[A] = [A]_p/K_A[Z_A]$ and $[B] = [B]_p/K_B[Z_B]$. In this case, Eqn (39) transforms into

$$[ABZ_{AB}] = \frac{K_{AB}[Z_{AB}][A]_p[B]_p}{K_A K_B [Z_A][Z_B] + K_{AB}[A]_p[B]_p}. \quad (40)$$

The rate of reaction (37) is $W_{AB} = k_{AB}[ABZ_{AB}]$, whence the apparent rate constant at low concentrations is

$$k_{AB} = \frac{W_{AB}}{[A]_p[B]_p} = \frac{k_{ZAB}K_{AB}[Z_{AB}]}{K_A K_B [Z_A][Z_B] + K_{AB}[A]_p[B]_p}. \quad (41)$$

According to this equation, the constant k_{AB} decreases with increase in both $[A]_p$ and $[B]_p$.

It is known that the second-order reactions require rapid mixing of the reactants in solution in polymers and they were

therefore investigated in amorphous polymers — atactic polypropylene and polyisobutylene — samples of which, each containing one of the two reactants, were mixed by repeated pressing. The experiments showed that the apparent rate constant for the reaction of benzoyl peroxide with dibenzyl sulfide varies with the concentration of each reactant and passes through a minimum (Fig. 15). This relation can be regarded as the sum of the curves described by Eqns (38) and (41).^{42, 43} In polyisobutylene, in which the solubilities of the reactants {and apparently the values of $[Z_A]$ and $[Z_B]$ } were 1.6 times lower than in polypropylene (the solubilities of benzoyl peroxide in these polymers at 50 °C were $S_A = 0.15$ and 0.23 , whilst those of dibenzyl sulfide were $S_B = 0.32$ and 0.54 mol kg^{-1} respectively), the minimum rate constant was observed at lower concentrations of the reactants.

The existence of two reaction paths [reactions (35), (36), and (37)] has also been confirmed by qualitative experiments: the 'inert' phenyl benzoate, which does not participate in the reaction, substitutes a molecule of benzoyl peroxide in the sorption centres

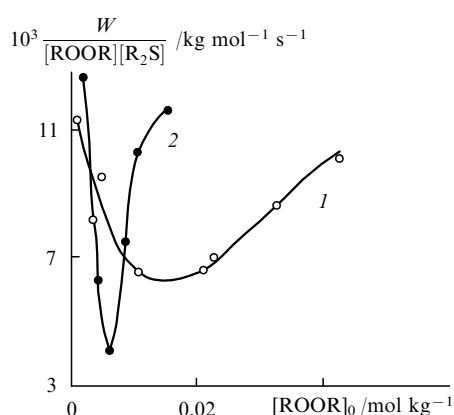


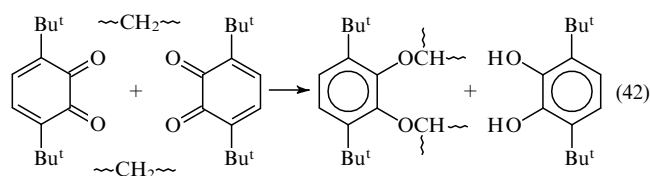
Figure 15. Dependence of the effective rate constant of the reaction of benzoyl peroxide with dibenzyl sulfide in atactic polypropylene (I) and polyisobutylene (2) on the initial peroxide concentration $[ROOR]_0$ (temperature is 50 °C).⁴³

of both types — $[Z_A]$ and $[Z_{AB}]$ — and lowers the rate of reaction in the region of low concentrations, when the mechanism of the pseudounimolecular conversion of the complexes ABZ_{AB} [reaction (37)] predominates, and accelerates the reaction at high concentrations, displacing the peroxide (and possibly also the sulfide) from complexes of the type AZ_A and BZ_B and increasing thereby the concentrations of the mobile molecules participating in reactions (35) and (36).

It is of interest that the rate of interaction of benzoyl peroxide with dibenzyl sulfide in polypropylene may be higher than the rate of the same reaction in its low-molecular analogue — isooctane, where the rate constant is independent of the initial concentration and is $(13.2 \pm 0.3) \times 10^{-3} \text{ litre mol}^{-1} \text{s}^{-1}$ under the same conditions (50 °C).

The slight increase of the rate constant for the bimolecular interaction of a phenolic antioxidant — 2,2'-methylenebis(6-*tert*-butyl-4-methylphenol) — with stearic acid as its concentration in polypropylene increases has been noted.⁴⁵

As an example of reactions of the type $2A + \text{polymer}$ the interaction of substituted *o*-benzoquinones with polyethylene and polypropylene have been studied.^{46, 47}



According to the Scheme (42), the reaction is accompanied by cross-linking of the polymer, the yield of substituted catechol amounting to 50%–60%. Assuming that a reaction of this kind may proceed only in large centres, each accommodating two reactant molecules, and replacing all B by A in Eqn (41), we obtain

$$W = \frac{k_{ZAA} K_{AA} [Z_{AA}] [A]_A^2}{K_A^2 [Z_A]^2 + K_{AB} [A_p]^2} \quad (43)$$

According to Eqn (43), the rate of reaction tends rapidly to the limit $k_{ZAA} [Z_{AA}]$ *i.e.* becomes independent of the concentration of the quinone. On the other hand, as the concentration of the quinone increases, the initial rate of reaction tends to a limit in accordance with Eqn (43) (Fig. 16).⁴⁶

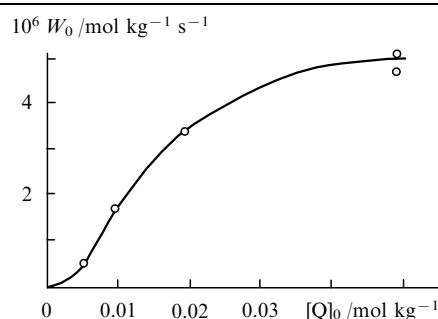


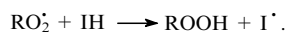
Figure 16. Dependence of the initial rate of reaction between 3,6-di-*tert*-butyl-1,2-benzoquinone (Q) and atactic polypropylene on the initial quinone concentration in the polymer (temperature is 180 °C).⁴⁶

In isotactic polypropylene, the initial rate of reaction is directly proportional to the initial quinone concentration, but a zero reaction order with respect to the quinone is observed in the course of the reaction over a long period of the latter.⁴⁷ Apparently the reaction in this 'rigid' polymer proceeds mainly in the centres formed as a result of the rearrangement of the polymer structure, similarly to the rearrangement described above (see Section V).^{30–32} Apparently the reactions in polyethylene and ethylene–propylene copolymers proceed in accordance with the same law.⁴⁸

X. Displacement catalysis and nonchemical synergism

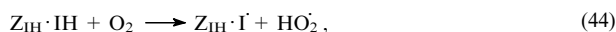
It has been shown³⁸ that the rate of thermal decomposition of benzoyl peroxide in isotactic polypropylene increases when phenyl benzoate, 'inert' in relation to this reaction in low-molecular media, is introduced into the polymer. Similarly, the rate of isomerisation of dimethylbenzylsilyl peroxide increases in the presence of the isomerisation product.³⁹ This phenomenon, associated with the displacement of the reactant molecules from centres more 'convenient' for them, the filling of which prevents a change in the shape or size of the reactant molecules necessary for the occurrence of the reaction, has been called³⁸ 'displacement catalysis'.

The main reaction on which the inhibition of oxidation is based — chain termination processes by the antioxidant (IH) — proceeds in accordance with the scheme



In polymers, the radicals (more correctly the macroradicals) $\text{RO}_2^\cdot$ cannot move freely and, for the occurrence of reaction (12), it is essential that the molecules of IH should possess translational mobility. Evidently the complexes between the antioxidant and the sorption centres $\text{IH} \cdot \text{Z}_{\text{IH}}$ are also immobile and the chain termination reaction must be preceded by the liberation of the IH molecule from the sorption centre.

Conversely, mobile oxygen molecules participate in the main side reaction — direct oxidation of IH — which leads to accelerated consumption of the antioxidant. Evidently the rate of oxidation of IH molecules in the centres 'convenient' for IH, *i.e.*



is lower than the rate of oxidation of the same molecules outside the sorption centres, *i.e.*



but in all cases the fraction of mobile molecules is small. Subsequently the $\text{I}^\cdot$ and $\text{HO}_2^\cdot$ radicals participate in a wide variety of reactions, most of which reduce the effectiveness of the inhibition of the process, for example $\text{HO}_2^\cdot + \text{IH} \rightarrow \text{H}_2\text{O}_2 + \text{I}^\cdot$. By increasing the fraction of mobile molecules, it is possible to increase selectively the rate of chain termination, altering slightly the rate of the undesirable stages of the process.

According to Eqn (21), substance B, which is relatively resistant to oxidation and reactions with peroxy-radicals but is capable of displacing IH from the centres Z_{AH} , may increase the fraction of mobile IH molecules at the same or even smaller overall concentration of the antioxidant. Assuming for simplicity that all the molecules of B are present in the polymer as complexes with Z_{AH} we find

$$[\text{IH}] = \frac{[\text{IH}]_{\text{hp}}}{K_{\text{AH}}\{[\text{Z}_{\text{AH}}] - [\text{B}]_{\text{p}}\}}. \quad (46)$$

The apparent chain termination rate constant is related to the true constant k_t for the $\text{IH} + \text{RO}_2^\cdot$ reaction by the expression

$$k_{\text{t}} = \frac{k_{\text{r}}}{K_{\text{AH}}\{[\text{Z}_{\text{AH}}] - [\text{B}]_{\text{p}}\}}. \quad (47)$$

Experiments have shown that comparatively 'inert' substances such as phenyl benzoate, octamethylcyclotetrasiloxane, and heptadecane (a low-molecular hydrocarbon) increase appreciably the effectiveness of phenolic antioxidants, distinct maxima appearing on the composition–induction period (*i.e.* the period of the effective retardation of the oxidation reaction) curve obtained at a constant overall concentration of the additives (Fig. 17). In contrast to the similar effect induced by chemically reactive additives, we called this phenomenon 'nonchemical synergism'.^{49–51} At high concentrations, the 'inert' additive disrupts the structure of the polymer and, in contrast to the usual 'chemical' synergism, the effect involving an increase in effectiveness vanishes.⁵²

It is seen from Fig. 18⁵² that, when an 'inert' additive such as octamethylcyclotetrasiloxane (at a variable concentration) is introduced into polypropylene containing phenyl- β -naphthylamine (PNA) as the antioxidant (at a constant concentration), the concentration of substance A in the gas phase initially increases owing to its displacement [Eqn (21)] and then decreases as a result of the rearrangement of the sorption centres {the increase in $[\text{Z}_k]$ } and then again increases owing to the displacement of A but this time from the new centres. This phenomenon is satisfactorily reproduced for various pairs of dissolved substances (see, for example Shlyapnikov *et al.*⁵⁰).

Thus the elements of topological disorder, *i.e.* the various entanglements of monomer chains, behave in polymers as quasi-

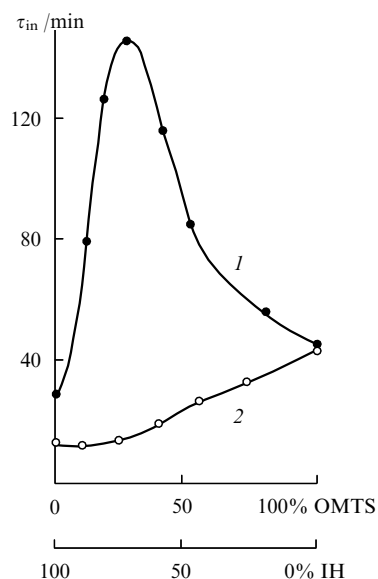


Figure 17. Dependence of the induction period in the oxidation of polyamide 12 on the composition of a mixture of 2,2'-methylenebis(6-*tert*-butyl-4-methylphenol) (IH) and octamethylcyclotetrasiloxane (OMTS) at 170 °C (1) and 190 °C (2). Overall concentration of additives 0.02 mol kg⁻¹ oxidant — oxygen, pressure — 300 mmHg.⁵¹

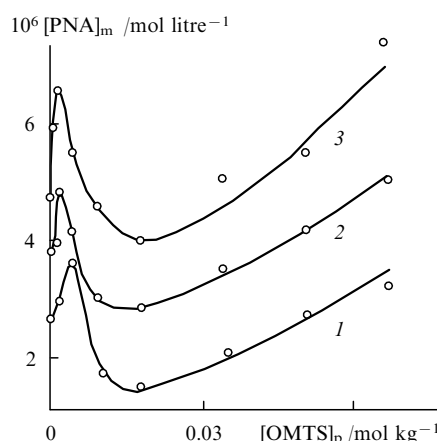


Figure 18. The concentration of phenyl- β -naphthylamine in the gas phase $\{[\text{PNA}]_{\text{m}}\}$ over polyethylene as a function of the concentration of octamethylcyclotetrasiloxane at different temperatures (°C): (1) 180; (2) 190; (3) 200 $\{[\text{PNA}]_{\text{p}} = 0.08 \text{ mol kg}^{-1}\}$.⁵²

molecules differing in their properties and reactivity from the polymeric substance surrounding them.

XI. The zone model of the oxidation of polymers

The presence in the sorption centres Z_i of a free volume sufficient, on the one hand, to accommodate the molecules of low-molecular substances, including oxygen, and, on the other hand, sufficient for the formation of an activated complex in the $\text{RO}_2^\cdot + \text{RH}$ and $\text{R}^\cdot + \text{O}_2$ reactions may lead to a significant difference between the reactivities of the polymeric substance present in the centres Z_i and the surrounding polymeric substance in which short-range order is maintained. It may be postulated that oxidation reactions proceed only in such centres and that a free valence is transferred from centre to centre either as a result of migration along the polymer chain⁵³ or as a result of the diffusion of light radicals.⁵⁴ We shall consider the consequences of this model.^{3,55}

Suppose that a single free valence, responsible for the formation of the radical $\text{RO}_2^\cdot$, enters a zone having a volume v_z with the concentration of monomer units $[\text{RH}]_{\text{z}}$ and a sufficient con-

centration of oxygen, which converts the radicals $R^\bullet$ into $RO_2^\bullet$. The concentration of the radical $RO_2^\bullet$ in the zone is $[RO_2^\bullet]_Z = 1/v_Z$. The consumption of the reactive groups $[RH_Z]$ in the zone is described by the equation

$$-\frac{d[RH]_Z}{dt} = \frac{k_2[RH]_Z}{v_Z}, \quad (48)$$

where

$$[RH]_Z = ([RH]_0) \exp\left(\frac{-k_2 t}{v_Z}\right). \quad (49)$$

According to Eqn (49), the reactive substance is almost fully consumed during the time $\tau \approx 5v_Z/k_2$.

Next there is a possibility of two versions of the development of the process. If the residence time of the free valence in a single zone is $\vartheta \leq \tau$, then the free valence migrates from zone to zone faster than the substance of the zone is consumed. In this case, the rate of reaction is determined by the elementary constants k_1 , k_2 , etc. and the only difference between the kinetics of the reaction and the kinetics of the oxidation of low-molecular liquids is the incomplete consumption of the substance being oxidised: after the consumption of the substance, present in disturbed-order zones, the process is strongly retarded or comes to a complete stop. On the other hand, if $\vartheta \gg \tau$, then the free valence remains in the zone also after the consumption of the reactive substance contained in it and the rate of reaction is given by

$$W = \frac{v_Z[RH]_Z[RO_2^\bullet]}{\vartheta}. \quad (50)$$

The observed chain transfer rate constant $(k_2)_{\text{eff}}$ is described by the expression

$$(k_2)_{\text{eff}} = W[RO_2^\bullet][RH] = \frac{v_Z[RH]_Z}{[RH]\vartheta}, \quad (51)$$

i.e., subject to the assumptions made above, the experimentally observed constant $(k_2)_{\text{eff}}$ does not depend explicitly on the true elementary constants (including the chain propagation constant k_2).

The observed (effective) chain termination rate constant can be determined similarly. The rate of chain termination is equal to the frequency with which two free valences enter a single zone minus the rate of liberation of the unreacted valences from the zone, i.e.

$$W_t = 2 \frac{(1-\chi)[RO_2^\bullet]^2}{[Z]\vartheta} = 2(k_t)_{\text{eff}}[RO_2^\bullet]^2, \quad (52)$$

where $[Z]$ is the concentration of the zones and χ is the probability that a pair of free valences which have entered a single zone will leave it without recombination. If the value χ is sufficiently small, then the effective chain termination rate constant is given by

$$(k_t)_{\text{eff}} = \frac{2}{[Z]\vartheta}. \quad (53)$$

According to the proposed model, the local concentrations of low-molecular substances in the zones (sorption centres) may exceed by a large factor the average concentrations of these compounds in the polymer, which explains the strong influence of antioxidants⁵⁶ and oxygen^{57,58} on the yield of radicals from the 'cage' formed on decomposition of the hydroperoxy-group.

The zone model is illustrated by the scheme shown in Fig. 19.

The characteristic features of the extensive oxidation of a number of polymers may serve as confirmation of the model. Thus the rate of the high-temperature oxidation of polymers is second order with respect to the RH groups being oxidised:⁵⁸

$$W_{O_2} = \frac{k_1 k_2 k_3 [RH]^2 [O_2]}{2k_{3a} k_t} = k_e [RH]^2, \quad (54)$$

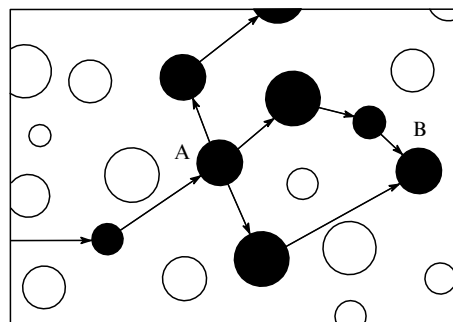
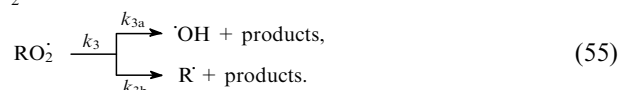


Figure 19. Schematic illustration of the propagation of the reaction in the polymer; open circles — zones of order violation before reaction; filled circles — ditto after reaction; A — chain branching site; B — chain termination site.

where k_3 is the rate constant for the decomposition of the radical $RO_2^\bullet$:



Assuming that not the entire polymer but only a proportion of its monomer units $[RH^*] = v_Z[Z][RH]_Z$ participate in the oxidation reaction and that q oxygen molecules are consumed per mole of the groups RH, one can formulate the following equation:

$$-\frac{d[RH^*]}{dt} = k_e [RH^*]^2 = k_e \left([RH^*]_0 - \frac{N_{O_2}}{q} \right)^2, \quad (56)$$

the solution of which gives

$$\frac{1}{[RH^*]_0 - N_{O_2}/q} - \frac{1}{[RH^*]_0} = k_e t.$$

Calculations have shown that, for the transformation of experimental oxygen absorption curves into straight lines in terms of the variables of Eqn (56), it is necessary to assume that $[RH^*]_0 \ll [RH]_0$, i.e. that only a small proportion of the volume of the polymer is oxidised. Under these conditions, q was assumed to be unity, since no other real values of q permit the assumption that $[RH^*]_0 = [RH]_0$. In particular, in the oxidation of polyamide 12 (the concentration of the monomer units is $5.076 \text{ mol kg}^{-1}$ and that of CH_2 groups is $55.8 \text{ g-equiv. kg}^{-1}$) the transformation of kinetic curves requires the assumption that $[RH^*]_0 = 0.6 \text{ mol kg}^{-1}$ (Fig. 20).⁵⁹ As can be seen from the figure, the

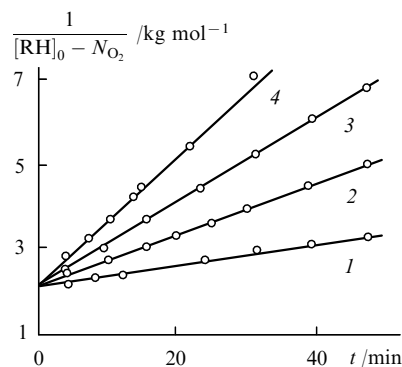


Figure 20. Variation of the concentration of the reactive part of the polymer during the oxidation of polyamide 12 (200 °C, oxygen) in coordinates for a second-order reaction (according to data of Monakhova *et al.*⁵⁹) at different pressures (mmHg); (1) 50; (2) 150; (3) 310; (4) 510. In the calculations, it was assumed that $[RH^*] = 0.6 \text{ mol kg}^{-1}$.

straight lines referring to different oxygen pressures intersect at a single point, *i.e.* the fraction of the substance being oxidised $[RH^*]_0$ is independent of the O_2 pressure.

XII. Conclusion

It follows from the data described that there exists a series of processes in which the elements of topological disorder present in the polymeric substance may be regarded as species which differ to some extent in their properties and reactivity from the relatively ordered substance surrounding them and that the distribution of the elements of disorder in the polymeric substance can be regarded as a negative image of its morphological (supermolecular) structure.³ Therefore, if the disorder is not taken into account as a separate component, the properties of the polymer will not be an unambiguous function of its composition and molecular mass distribution.

We believe that purpose-directed formation of topological structures in a polymeric material would be the next natural step in the physical chemistry of polymers and in the technology of polymeric materials.

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^a — *Dokl. Chem. Technol., Dokl. Chem. (Engl. Transl.)*

^b — *Russ. J. Chem. Phys. (Engl. Transl.)*

^c — *Polym. Sci. (Engl. Transl.)*

^d — *Russ. Chem. Bull. (Engl. Transl.)*

^e — *Kinet. Catal. (Engl. Transl.)*

^f — *Russ. J. Phys. Chem. (Engl. Transl.)*

Methods of synthesis of deuterium-labelled lipids

N A Bragina, V V Chupin

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Abstract. The review deals with the methods of synthesis of deuterium-labelled hydrophobic and hydrophilic synthons of lipid molecules and the routes to selectively and perdeuterated phospholipids and their analogues. Deuterium-labelled lipids are used to study the structural organisation and functioning of biological membranes including NMR studies and neutron diffraction of lipid–lipid and lipid–protein interactions. The bibliography includes 145 references.

I. Introduction

The explosive development of molecular biology, particularly of biomembranology, has stimulated research aimed at the synthesis of deuterated lipids. The preparation of selectively and perdeuterated lipids has permitted studies of structural organisation and functioning of biological membranes. Deuterium can be selectively incorporated into any methyl, methylene, or methine group of the lipid molecule. In these transformations, the properties of lipid molecules remain unchanged, which makes the deuterium label superior to spin or fluorescent labels.

Originally, the deuterium-labelled lipids were used only in mass spectrometry for the analysis of pathways of fragmentation of lipid molecules.^{1,2} In the 70–80's, novel procedures for the study of the structural organisation of membranes were developed, such as solid-state ²H NMR^{3–6} and neutron diffraction.^{7–9}

However, these methods are not very sensitive and require large quantities of lipid samples (tens and even hundreds of milligrams). Thus, the development of convenient (in the preparative sense) methods of synthesis of deuterium-labelled lipids that would permit preparation of these lipids in the amounts required is still urgent.

Another trend in the use of deuterated lipids is related to studies into the structure of membrane proteins. Secondary and tertiary structures of membrane proteins are determined by the

traditional method of high-resolution two-dimensional ¹H NMR spectroscopy.¹⁰ Obviously, such studies require perdeuterated detergents that are 'transparent' for the ¹H NMR method. Organic solvents or micelles obtained from lipid-like detergents are generally used as the membrane environment.^{11–14} Yet no ¹H NMR studies into the structure of membrane proteins in lipid bilayers have thus far been carried out because, in contrast to small-sized micelles, the movement in bilayers is anisotropic, which results in significant broadening of signals in the NMR spectra. The principal conditions for the study of secondary and tertiary structures of proteins in lipid bilayers have now been established. The possibility of obtaining high-resolution two-dimensional ¹H NMR spectra of lipid bilayers using the magic-angle spinning method has been demonstrated.^{15,16} Studies into the structure of intramembrane proteins are being scheduled. The accessibility of perdeuterated lipids is a prerequisite for conducting these studies.

The present review describes the methods of synthesis of deuterium-labelled hydrophobic and hydrophilic precursors of lipid molecules and of selectively perdeuterated phospholipids and their analogues.

The methods for the incorporation of deuterium are based on the use of commercially available deuterium-containing chemical reagents,¹⁷ such as heavy water (D₂O), alcohols (MeOD), acids (D₂SO₄), or bases (NaOD). Enolisable protons of lipids can be specifically exchanged for deuterium under conditions of acid or base catalysis. Molecular deuterium in combination with platinum or palladium catalysts and Raney nickel is mostly employed for conducting a non-specific exchange.

LiAlD₄, NaBD₄ and their derivatives are most often used for the specific reduction of particular functional groups. The use of molecular deuterium has not found wide application in the catalytic reduction of double and triple bonds, since the reduction is often accompanied by a non-selective proton–deuterium exchange.

Bacterial strains that are unable to synthesise certain lipid components and that are grown on media containing these components with deuterium labels are used for specific incorporation of deuterium. Non-specific deuteration is achieved by growing bacteria on culture media in which heavy water is used instead of H₂O.

The final assembly of deuterium-containing fragments into synthons needed for phospholipid synthesis is performed by

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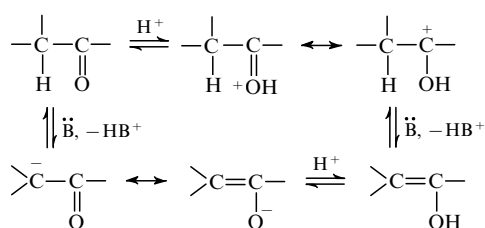
methods of organic synthesis. Phospholipids are synthesised by traditional methods employed in lipid chemistry.

II. Synthesis of deuterated fatty acids

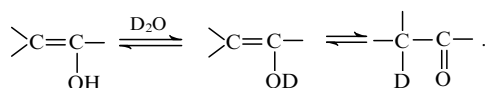
The simplest (in the preparative sense) methods for obtaining selectively and perdeuterated fatty acids are based on the reaction of proton–deuterium exchange.¹⁷ A prerequisite for conducting such reactions is the presence of a medium with readily dissociating deuterons and a catalyst enabling the dissociation of C–H bonds of fatty acids.

As a rule, such reactions are carried out at sufficiently high temperatures; fatty acids with C–D bonds are obtained after removal of the catalyst. Under conditions close to physiological ones, they are stable and do not enter into the reactions of reverse exchange. If fatty acid molecules contain functional groups that increase the acidity of vicinal C–H bonds, the exchange can be carried out selectively.

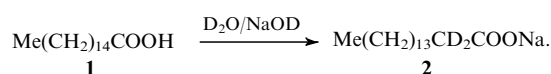
In particular, protons at the α -position to a carbonyl or a carboxyl group can be easily exchanged for deuterium. A tautomeric transformation shown in Scheme 1 is characteristic of carbonyl compounds.



The formation of an enol tautomer occurs either in the presence of bases *via* the enolate anion or in the presence of acids *via* the carbocation.¹⁸ If these transformations are carried out in an excess of a solvent containing readily dissociating deuterons, α -protons exchange for deuterium.



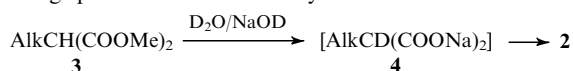
Let us consider some examples of such a selective exchange. The presence of a carboxyl group in palmitic acid **1** increases the acidity of α -protons; selective exchange of α -protons for deuterium gives compound **2** in D_2O (the source of mobile deuterons) in the presence of a base as the catalyst.



In case of long-chain fatty acids, the reaction proceeds under relatively drastic conditions (200 °C, 72 h, 1% NaOD).¹⁹ α -Protons of short-chain carboxylic acids undergo the exchange more readily.²⁰

This approach can be used for the incorporation of deuterium into fatty acids with one double bond without the migration of this bond along the hydrocarbon chain.²¹

Fatty acid esters are more reactive than the acids themselves. Thus equilibrium conditions for the exchange of α -protons of methyl palmitate are reached within several hours of boiling in MeOD in the presence of NaOD.^{22–24} With the same ease, the exchange proceeds with monoalkyl malonates **3**.

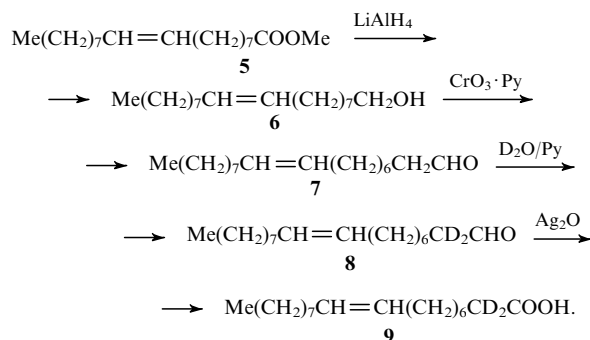


Alk = Me(CH₂)₁₃.

The exchange takes place on boiling in D_2O (which is a more readily available reagent than MeOD) in the presence of NaOD as the catalyst.^{24, 25} Decarboxylation of the sodium dicarboxylate **4**

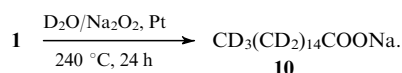
results in a salt of the monocarboxylic acid **2** deuterated at the α -position.

In aldehydes, the exchange of α -protons occurs very readily, which can be used in exchange reactions aimed at deuterium incorporation at the α -position of relatively labile, unsaturated fatty acids. The synthesis of [2,2-²H₂]-oleic acid **9** is an example.²⁶ Methyl oleate acid **5** served as the starting material. It was first reduced to the alcohol **6** which was then oxidised to the aldehyde **7** followed by the exchange reaction in $\text{D}_2\text{O}/\text{Py}$. [2,2-²H₂]-Oleic acid **9** was obtained by the oxidation of the aldehyde **8** with silver oxide.



The multistep character of this approach is its obvious limitation.

Exchange reactions are also used for the substitution of non-enolisable protons for deuterium. Complete non-specific exchange of protons in palmitic acid **1** is achieved at high temperatures and pressure in the presence of Pt and Na₂O₂ as the catalysts.²⁷

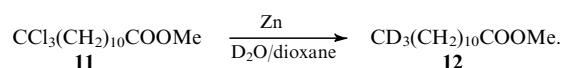


Under these conditions, partial decarboxylation of a fatty acid occurs, the yield of the deuterated product **10** is 80%–85%.

Fully deuterated acids can also be obtained by passing gaseous deuterium through a suspension of palladium black in a fatty acid.²⁸ The specificity of the exchange of non-enolisable protons is rather low. However, in some cases selective proton–deuterium exchange can be achieved. If the reaction is carried out under closely controlled conditions, it is possible to exchange predominantly the protons of the terminal methyl group of a carboxylic acid.²⁹ In this case, K₂PtCl₄ is used as the catalyst.

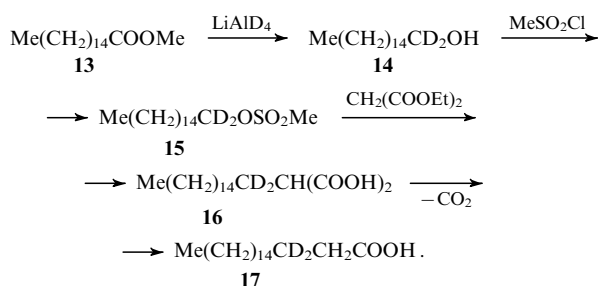
The obvious merit of the above methods is that the synthesis of deuterated fatty acids does not require complex multistage procedures. Moreover, it allows the use of available fatty acids as the initial material. The reactions occur with high yields. The final products are isolated by extraction without recourse to chromatographic purification. The extent of deuteration of a fatty acid depends on the number of repetitions of the exchange procedure, the nature of the deuterating reagent, and its excess. In order to increase the extent of deuteration of the target fatty acids and achieve a more rational use of expensive deuterated solvents, exchange reactions are usually carried out in 2–3 steps.

The preparation of selectively deuterated fatty acids requires the use of more sophisticated procedures. They combine the exchange reactions, selective reduction, and the synthesis of fatty acids from individual synthons. The synthesis of methyl laurate **12** having a deuterated methyl group at the end of the hydrocarbon chain has been described.²⁵ Methyl 12,12,12-trichlorododecanoate **11** was used as the starting material. Zinc dust in D_2O –dioxane specifically reduces the CCl₃ group of the ester **11** to CD₃ resulting in the product **12**.

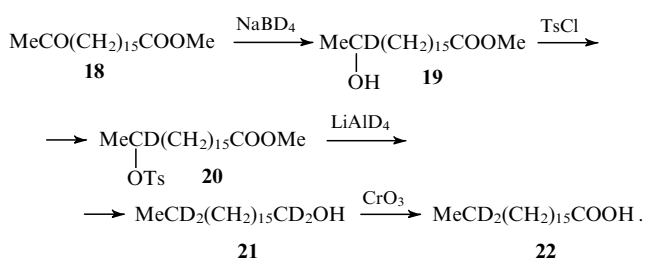


The methyl ester **12** can be reduced to the corresponding alcohol and used to obtain labelled myristic acid.^{30,31}

Reduction with LiAlD₄ and NaBD₄ is extensively used for the selective incorporation of deuterium labels into different positions of hydrocarbon chains of fatty acids. In this case, deuterium incorporation is carried out in one step and the extent of deuteration of the final products depends exclusively on the extent of deuteration of LiAlD₄ or NaBD₄ used in this reaction. This method has been used for the synthesis of [3-²H₂]-stearic acid **17**^{19,32} from methyl palmitate **13** as the starting compound. It was reduced to the alcohol **14** with LiAlD₄, and then the hydrocarbon chain was elongated by a malonate approach. To this end, the alcohol **14** was activated by its conversion into the mesyl derivative **15**, which was used as the alkylating reagent. The alkylation of the diethyl malonate under alkaline conditions is accompanied by saponification of ester groups; subsequent decarboxylation of the dicarboxylic acid **16** gives the acid **17** with a deuterium label at the β-position.



Apparently, any oxo group in the hydrocarbon chain can be selectively reduced to the CD₂ group.^{19,33} Thus the methyl ester of the oxo acid **18** was selectively reduced with NaBD₄ to the hydroxy ester **19**. The latter was further converted into the tosylate **20** and reduced with LiAlD₄, which resulted in the alcohol **21** deuterated at positions 1 and 17. The oxidation of the alcohol **21** with chromium oxide was accompanied by the removal of deuterium from the position 1, eventually resulting in [17-²H₂]-stearic acid **22**.

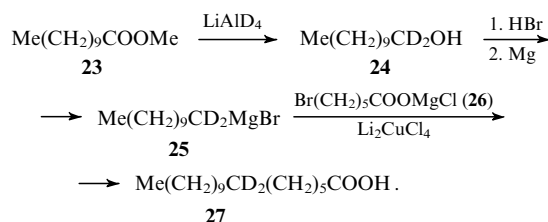


The same scheme can be used for the stereospecific incorporation (if required) of one deuterium atom into the fatty acid molecule.³³

In addition to the tosylates of the type **20**, the synthesis of deuterated fatty acids makes use of mesylates and iodides, which are also reduced with LiAlD₄.^{34,35} Primary and secondary bromides are not reduced,^{35,36} which makes it possible to obtain the necessary synthons for the fatty acid synthesis. However, the selectivity of LiAlD₄ is rather low. Therefore, another reducing agent, NaBD₃CN, has been recommended.³⁷ This compound selectively reduces tosylates, mesylates, and iodides in the presence of ester groups in aprotic solvents.

The CD₂ groups are obtained by the Clemmensen reduction of oxo groups (Zn/DCl).^{32,38} However, the presence of mobile deuterons in the reaction medium results in the exchange of the protons at the α-position relative to the oxo group, which leads to the formation of the (CD₂)₃ fragment in the hydrocarbon chain. A versatile procedure has been developed³⁹ for the substitution of the CH₂ group by CD₂ at any position of the saturated fatty acid. This method consists in the reduction of the corresponding ester of

the carboxylic acid **23** with LiAlD₄. The alcohol formed **24** is converted into the bromide, and the bromide is used to obtain the Grignard reagent **25**. The interaction of the Grignard reagent **25** with a salt of a bromo-substituted carboxylic acid **26** in the presence of Li₂CuCl₄ as a catalyst gives the carboxylic acid **27** with a deuterated methylene group. At this stage, the reaction proceeds in high yields (77%–85%) which tend to decrease with the elongation of the hydrocarbon chain in the compound **25**.



By varying the length of the hydrocarbon chain of the ester **23** and the bromo-substituted acid **26**, one can obtain fatty acids with variable lengths of the hydrocarbon chain and variable positions of the CD₂ group.

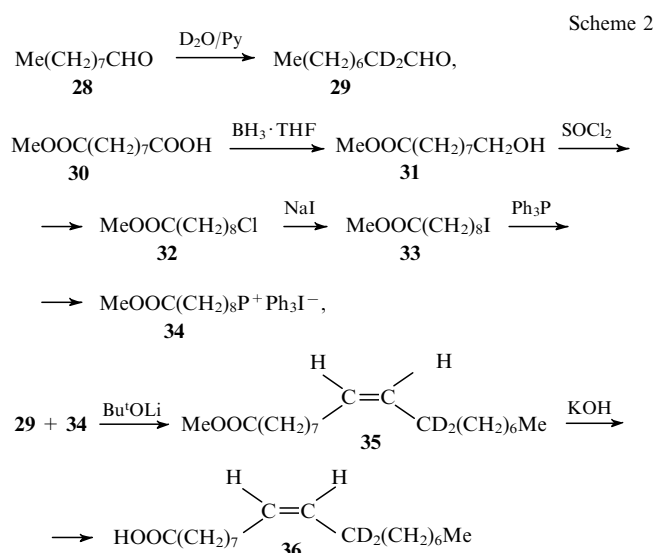
Lithium dimethylcuprate, LiCuMe₂, was used for the substitution of the tosyl group by the methyl group in the synthesis of methyl [13-²H₂]-myristate.⁴⁰

Vicinally deuterium-labelled fatty acids are synthesised by the reduction of multiple bonds with gaseous deuterium on platinum and palladium catalysts.^{41,42} This method for deuterium labelling is rarely used due to a number of disadvantages, such as the necessity to use a large excess of deuterium, drastic reaction conditions, and, which is the most important, because of the side reactions of isotope exchange. The use of the homogeneous Wilkinson catalyst, [tris(triphenylphosphine)rhodium chloride], allows one to avoid side reactions to some extent.^{43–46} Double and triple bonds can be reduced on a deuterated Raney nickel.^{47,48} However, the most popular procedure for the catalytic hydrogenation of double and triple bonds with molecular deuterium is the deuteration of triple bonds on the Lindlar catalyst. The lower activity of the Lindlar catalyst in comparison with other catalysts makes it possible to selectively deuterate triple bonds. This reaction proceeds with a high degree of stereoselectivity; the content of the *cis*-isomer (the natural isomer in unsaturated fatty acids) in dideuterated alkenes amounts to 98%–99%. This method was used in the synthesis of octadeuterioarachidonic acid⁴⁹ and a series of unsaturated CD=CD-fatty acids.^{49–53} Reduction on the Lindlar catalyst is also used in 'alkyne' syntheses of unsaturated fatty acids with deuterium-labelled methylene fragments, since no reverse deuterium–proton exchange takes place under conditions of catalytic hydrogenation.²¹

Selective deuteration of the double bonds of unsaturated fatty acids is also performed with deuteriohydrazine.^{32,54,55} This reaction is carried out only in the presence of small amounts of an oxidising agent (oxygen, sodium metaperiodate, hydrogen peroxide, copper(II) salts, etc.). First, the diimide DN=ND is formed *in situ* from deuteriohydrazine in the presence of the oxidiser; its *syn*-form ensures the *cis*-addition of deuterium to the double bond.⁵⁶

The synthesis of deuterium-labelled unsaturated acids is based on the use of the Wittig reaction.^{44,57–59} An example of such synthesis is shown in Scheme 2.

According to this scheme, deuterium is incorporated *via* the exchange reaction into the α-position of nonanal **28** upon boiling the aldehyde in a D₂O/pyridine mixture. The second component of the Wittig reaction is obtained by the selective reduction of monomethyl azelate **30** to the alcohol **31**; the hydroxyl group is then consecutively substituted by chlorine (compound **32**) and iodine (compound **33**), and the iodide **33** alkylates triphenylphosphine. The key step in this synthesis is the Wittig condensation of the aldehyde **29** and the phosphonium salt **34**. Initially, it was proposed to use sodium ethoxide in this reaction.⁵⁸ However, very often the condensation proceeded in very low yields.⁶⁰ Later,



Bu^tOLi was recommended as a base.⁵⁹ The latter was obtained by the interaction of equimolar amounts of *tert*-butyl alcohol and hexyllithium. In this case, the condensation of compounds **29** and **34** proceeded with a sufficiently high degree of stereoselectivity, the yield of [11-²H₂]-oleic acid (**36**) and its *trans*-isomer, [11-²H₂]-elaidic acid, reached ~70%. The ratio of *cis*- and *trans*-isomers was 95:5. The formation of *cis*- and *trans*-isomers in the Wittig reaction is a serious limitation of this method, since the separation of geometric isomers of fatty acids requires special chromatographic procedures.⁵⁷ The ratio of *cis*- and *trans*-isomers depends largely on the reaction conditions.⁶⁰ For example, by performing the reaction with potassium bis(trimethylsilyl)amide, one can increase the content of the *cis*-isomer up to 98%⁶¹ which is comparable with the stereopurity of alkenes obtained by hydrogenation of acetylenic compounds on the Lindlar catalyst.

In addition to the above-described methods of elongation of hydrocarbon chains (malonate synthesis, condensation with the use of copper catalysts, the Wittig reaction), other approaches are employed in the synthesis of deuterium-labelled acids that are traditionally used in fatty acid chemistry, such as the 'alkyne' synthesis,^{21, 35, 43, 62, 63} enamine synthesis,^{19, 34, 64} and Kolbe electrolytic synthesis.^{33, 65–67} Synthesis of various deuterium-labelled acids has been considered in a number of reviews.^{30, 31}

III. Synthesis of deuterium-labelled hydrophilic components of phospholipids

The hydrophilic part of phospholipid molecules includes choline, ethanolamine, serine, glycine, inositol, and some other residues.^{68, 69}

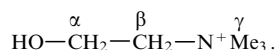
To study the structural peculiarities of the polar region of a lipid bilayer, various methods of synthesis of phospholipids with different deuterium-labelled polar portions of phospholipid molecules have been developed.

1. Synthesis of deuterated cholines

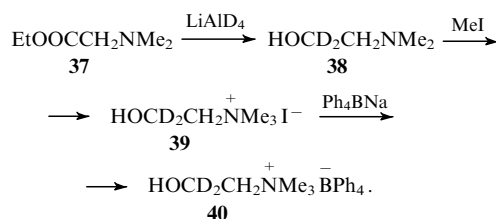
One of the most common phospholipids of biological membranes are phosphatidylcholines.⁶⁸ They are the favourite object for biophysical and biochemical studies. This is due to their ability to form stable bilayers within a broad range of temperatures, pH, and ionic strength. The quadrupole splitting of signals of deuterium labels in the ²H NMR spectra of choline is extremely sensitive to changes in the surface electric potential of the lipid bilayer,⁷⁰ which opens new opportunities for the study of electric properties of membranes. It is not surprising therefore that a great deal of attention has been given to the synthesis of deuterated cholines or their chemical precursors.

The developed methods to date permit the incorporation of deuterium into any part of the choline molecule. In order to define

the positions in the choline residue, we shall use the system of designations proposed by Seelig *et al.*:⁷⁰



In order to obtain choline labelled with deuterium at the α-position, the ethyl ester of *N,N*-dimethylglycine (**37**) is reduced with lithium aluminium deuteride, after which the *N,N*-dimethylaminoethanol (**38**) formed is subjected to methylation. This reaction gives [α-²H₂]-choline iodide (**39**),⁷¹ which is then condensed with 1,2-dipalmitoyl-*sn*-glycerophosphodichloridate to give 1,2-dipalmitoyl-*sn*-glycerophospho-[α-²H₂]-choline:

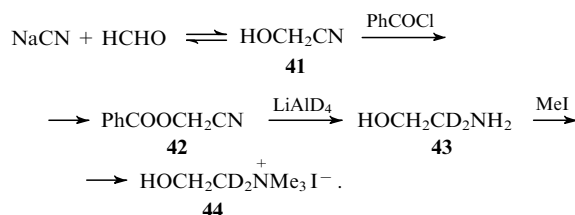


It should be noted that the condensation of phosphatidic acid or phosphodichloridate with choline is an important step in the synthesis of phosphatidylcholines. This reaction is carried out in organic solvents (usually, in pyridine, chloroform, dichloromethane, *etc.*). However, the solubility of choline iodide in organic solvents is very low, which is the reason for low yields at the stage of condensation of the phosphatidic acid and choline iodide. To overcome this problem, it was proposed to use choline acetate.⁷² However, the yields varied within a very broad range and were 40%–60% at best. This is also due to the relatively low solubility of choline acetate in organic solvents and its high hygroscopicity.

The synthesis of perdeuterated phosphatidylcholine was carried out with the use of a complex of choline iodide with iodine.⁷³ The drawback of this approach is the fact that this complex is unstable and loses iodine on storage or drying *in vacuo*. Moreover, after condensation it is necessary to remove the large excess of free iodine, whereas the yield of phosphatidylcholine is as low as 25%–40%.

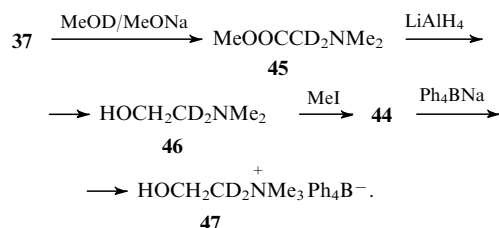
An effective approach to the synthesis of phosphatidyl choline has been proposed by Harbison and Griffin⁷⁴ who have used choline tetraphenylborate. A salient advantage of this method is that this salt is virtually insoluble in water, and choline can be easily and quantitatively isolated from aqueous solutions. The fact that choline tetraphenylborate is non-hygroscopic and is readily soluble in organic solvents, such as pyridine, allows one to achieve sufficiently high yields in its condensation with phosphatidic acid. [α-²H₂]-Choline tetraphenylborate (**40**) was prepared as follows. After methylation, the organic solvent was removed *in vacuo*, the residue was treated with aqueous alkali, insoluble aluminates were filtered off, and [α-²H₂]-choline was precipitated with an aqueous solution of sodium tetraphenylborate.

The synthesis of β-deuterated choline⁷¹ is based on the method earlier proposed for the synthesis of ¹⁴C-labelled ethanolamine.⁷⁵ According to this method, condensation of sodium cyanide with formaldehyde gives hydroxyacetonitrile (**41**), which is further benzoylated to give the nitrile **42**. The latter is reduced to [β-²H₂]-ethanolamine (**43**). Exhaustive N-methylation of [β-²H₂]-ethanolamine **43** gives [β-²H₂]-choline iodide (**44**):

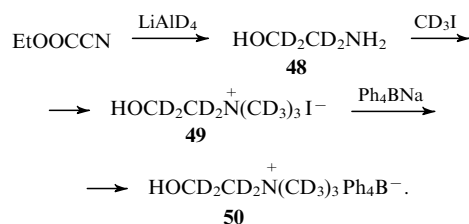


Yet another approach⁷⁶ consists in the use of the ethyl ester of *N,N*-dimethylglycine (**37**) as the starting compound. The mobile

α -protons of the compound **37** are exchanged for deuterium in MeOD in the presence of sodium methoxide. This exchange occurs at a high rate, and equilibrium conditions are reached within 1 h at room temperature. The deuterium exchange is accompanied by transesterification of the ethyl ester to give the compound **45**. The progress of the exchange reaction is easily monitored by following the disappearance of the signals corresponding to the CH₂ group and the appearance of signals of CHD and CD₂ groups in the ¹³C NMR spectra. The reduction of the methyl ester **45** to the corresponding alcohol **46**, its further methylation, and the preparation of [β-²H₂]-choline tetraphenylborate (**47**) are carried out in much the same way as the synthesis of the compound **40**, except that lithium aluminium hydride is used instead of lithium aluminium deuteride.

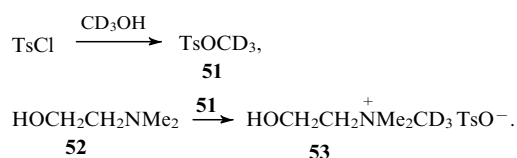


Per-C-deuterated choline⁷⁴ is obtained by reduction of ethyl cyanoacetate with lithium aluminium deuteride with subsequent exhaustive N-deuteromethylation of the deuterated ethanolamine **48**. The resulting choline iodide (**49**) can be converted into the acetate,⁷² the complex with iodine,⁷³ or tetraphenylborate (**50**).⁷⁴ The latter seems to be the most convenient form of choline for its subsequent condensation with phosphatidic acid. The total yield of choline tetraphenylborate **50** exceeds 40%.⁷⁴



In addition to this method, per-C-deuterated choline can be obtained by quaternisation of [2-²H₂]-trimethylamine with 1,1,2,2-[²H₄]-2-bromoethanol as in the synthesis of perdeuterated dodecylphosphocholine (see below).⁷⁷ Perdeuterated β-bromoethanol can be used in those schemes of phosphatidylcholine syntheses that envisage the formation of the choline residue at the last stage, by the reaction of bromo(chloro)alkanes with trimethylamine.⁷⁸

Choline with deuterated methyl groups is synthesised by the methods based on methylation of ethanolamine or its partly methylated derivatives. Methylation of ethanolamine followed by precipitation of choline as tetraphenylborate was used to obtain [γ-²H₃]-choline in a practically quantitative yield.⁷⁴ Choline tosylate is yet another convenient derivative for the phosphatidylcholine synthesis.⁷⁹ However, this choline salt is readily soluble in water. Moreover, choline tosylate cannot be obtained by a direct ion-exchange reaction between choline iodide and *p*-toluenesulfonic acid. The conversion of choline iodide into tosylate requires an intermediate synthesis of choline acetate.²⁴ *p*-Toluenesulfonyl chloride is the starting compound in the synthesis of [γ-²H₃]-choline tosylate (**53**).²⁴ Its reaction with CD₃OH yields methyl tosylate (**51**), which is further used for the deuteriomethylation of 2-*N,N*-dimethylethanolamine (**52**). Choline tosylate **53** is obtained in a quantitative yield:



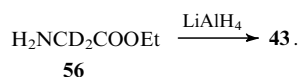
2. Synthesis of deuterium-labelled ethanolamines

Ethanolamine is the structural element of phosphatidylethanolamines, which, like phosphatidylcholines, are zwitterionic phospholipids. However, in contrast to phosphatidylcholines, phosphatidylethanolamines manifest basically different self-organisation properties. Under physiological conditions, phosphatidylethanolamines form in water inverted hexagonal structures rather than an extended bilayer.^{80,81} It is believed that the ability of phosphatidylethanolamines to form non-bilayer structures strongly affects many membrane functions.

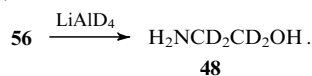
To obtain ethanolamines with deuterium labels in different positions, the reduction of glycine derivatives^{82–84} with metal deuterides is generally used. Thus the reduction of glycine ethyl ester (**54**) with lithium aluminium deuteride⁸³ results in ethanolamine (**55**) with a deuterium label at position 1.



An analogous procedure is used to synthesise ethanolamine **43** with a deuterium label at position 2. However, in this case the deuterated ethyl ester of glycine (**56**) and lithium aluminium hydride are used as the starting compounds.⁸³

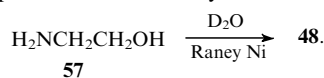


[2-²H₂]-2-Aminoethanol **43** can also be obtained by the methods employed in the synthesis of deuterated cholines.^{71,75} The ethyl ester of deuterated glycine **56** can also serve as the starting compound in the synthesis of [1,2-²H₄]-2-aminoethanol (**48**).⁸³



The latter was also obtained by the reduction of ethyl cyanoacetate according to the procedure for the synthesis of perdeuterated choline.⁷⁴

In addition to reduction, deuterated ethanolamines can be obtained by proton–deuterium exchange reactions. Thus Raney nickel in D₂O is used as the catalyst in the exchange of protons in ethanolamine (**57**).⁸⁵ This exchange is non-specific despite the higher activity of position 2. The indisputable advantage of this approach is undoubtedly the accessibility of the initial reagents.



The general methodology of the preparation and utilisation of ‘deuterated’ Raney nickel for proton exchange in aliphatic and aromatic compounds has been described by Pojer.⁸⁶

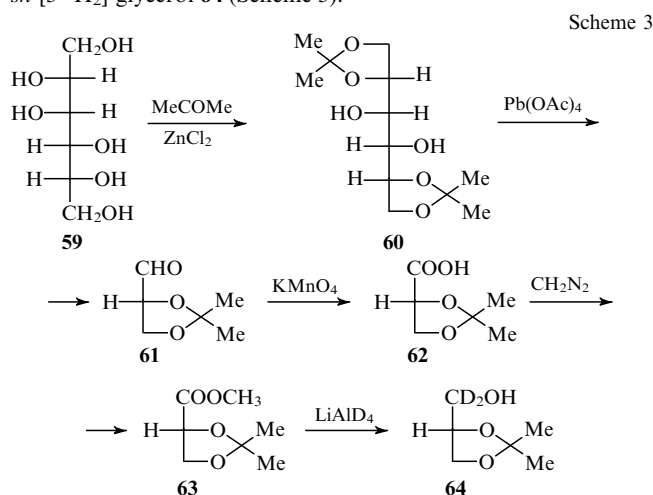
Deuterium-labelled ethanolamines are obtained in the form of water-soluble hydrochlorides and are routinely used in phosphatidylethanolamine synthesis by enzymic transphosphatidylation, which is catalysed by phospholipase D and takes place in aqueous media.

3. Synthesis of deuterium-labelled glycerols

Glycerol (**58**) is a structural element of all glycerophospholipids and a constituent of the polar region of the negatively charged phospholipid phosphatidylglycerol, which, in turn, is the structural component of cardiolipin (diphosphatidylglycerol). The interest in the synthesis of deuterated glycerols is associated not only with their use in the synthesis of labelled lipids, but also with studies of glycerol as a substrate and intermediate of many biosynthetic processes. In this connection, the synthesis of various deuterium-labelled glycerols has become the subject of a large number of publications.^{73,87–95} The methods elaborated to date allow one to obtain glycerols with a deuterium label at any

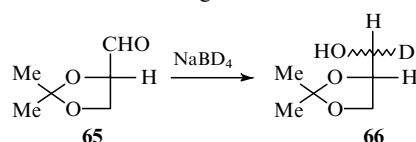
position of the molecule. Non-protected deuterium-labelled glycerols are used as substrates in enzymic syntheses of phospholipids, and their isopropylidene derivatives are used in chemical syntheses of phosphatidylglycerols. The necessary stereoconfiguration of isopropylidene-glycerols is provided by the original use of specific optically active reagents. Deuterium is introduced into the glycerol molecule by reduction with lithium aluminium deuteride, sodium borodeuteride, or their derivatives,^{73, 87–92} as well as by enzymic methods.^{87, 93, 94}

Let us consider the syntheses of various deuterated glycerols and their isopropylidene derivatives. 1,2-*O*-Isopropylidene-*sn*-[3-²H₂]-glycerol (**64**) has been synthesised by the method traditionally employed in lipid chemistry.⁸⁶ This method is based on the conversion of D-mannitol (**59**) into the 1,2:5,6-di-*O*-isopropylidene derivative **60** followed by scission of the vicinal diol group with lead tetraacetate. To remove the proton remaining at position 1, the protected D-glyceraldehyde **61** is oxidised to the corresponding glyceric acid **62**, which can further be reduced to the alcohol. For more optimal utilisation of the relatively expensive lithium aluminium deuteride, the acid **62** is converted into the methyl ester **63** prior to reduction to obtain 1,2-*O*-isopropylidene-*sn*-[3-²H₂]-glycerol **64** (Scheme 3).⁸⁷



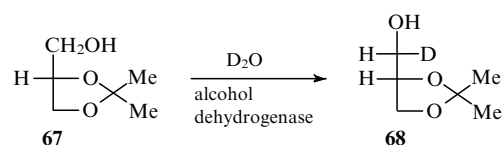
An approach, which is very similar to that described above, was used⁸⁸ in the synthesis of **64**, except that the oxidation of the vicinal diol **60** was performed with sodium periodate, the aldehyde **61** was oxidised with chromic acid, and the resulting acid **62** was directly reduced with lithium aluminium deuteride. Along with D- and L-mannitol, D- and L-serine are also used as the original optically active compounds.^{90, 91}

The synthesis of 2,3-*O*-isopropylidene-*sn*-[1-²H]-glycerol (**66**) has been described.⁸⁷ The aldehyde **65**, an enantiomer of the aldehyde **61**, was prepared from L-mannitol, which, in turn, was obtained by the reduction of L-mannose. The reduction of the aldehyde **65** with sodium borodeuteride gives the isopropylidene derivative **66** containing one deuterium atom at position 1.



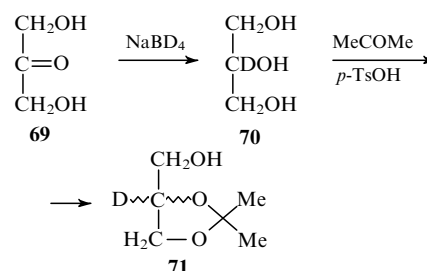
Unfortunately, the reduction of the aldehyde **65** is non-stereospecific, and the compound **66** is a mixture of two diastereomers.

The stereospecific incorporation of deuterium into glycerol is carried out by both chemical⁹¹ and enzymic^{87, 93, 94} methods. An original procedure⁸⁷ based on the enzymic reaction of proton–deuterium exchange has been proposed. In the presence of horse alcohol dehydrogenase, one of the protons of 1,2-*O*-isopropylidene-*sn*-glycerol (**67**) is stereospecifically exchanged in D₂O to give 1,2-*O*-isopropylidene-(3*R*)-*sn*-[3-²H]-glycerol (**68**).

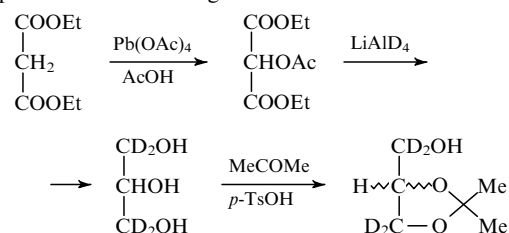


Apparently, this reaction is of general character and can be used for stereospecific exchange of one proton for deuterium in any primary alcohol. A combination of chemical and enzymic methods gave (1*R*, 2*R*)-[1,1-²H, ³H]-glycerol stereospecifically labelled with both deuterium and tritium.⁹³

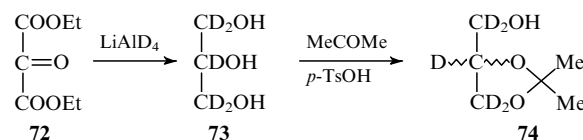
In order to incorporate deuterium into position 2 of the glycerol molecule, the reduction of dihydroxyacetone (**69**) with sodium borodeuteride is used.⁸⁷ When required, glycerol (**70**) can be converted into the isopropylidene derivative by the reaction with acetone in the presence of *p*-toluenesulfonic acid. However, this reaction gives racemic isopropylidene-glycerol (**71**):



Selective incorporation of deuterium into positions 1 and 3 of the glycerol molecule is achieved using the sequence of reactions depicted in the following scheme:⁸⁷



Perdeuterated glycerol **73** (mobile protons of the hydroxy groups are not taken into consideration) is prepared by the reduction of diethyl oxomalonate (**72**) with lithium aluminium deuteride.⁷³ Enzymic phosphorylation of the deuterated glycerol **73** ensures the necessary stereoconfiguration in subsequent intermediates of glycerophospholipid synthesis.⁷³ The introduction of the protecting isopropylidene group into the glycerol **73** gives racemic 1,2-*O*-isopropylidene-*rac*-[1,2,3-²H₃]-glycerol (**74**).⁸⁷



Deuterium-labelled glycerols and their isopropylidene derivatives are used in the synthesis of deuterium-labelled phosphatidylglycerols and perdeuterated phosphatidylcholine. The incorporation of deuterium into position 3 of 1,2-di-*O*-alkylglycerol has been described.⁹² The latter was oxidised to the dialkyl derivative of glyceric acid using the Jones reagent. The resulting acid was reduced with lithium aluminium deuteride to give 1,2-di-*O*-alkyl-[3-²H₂]-glycerol. The diglyceride component can further be used for the synthesis of phospho- or glycolipids. However, this method is inapplicable to the synthesis of diacyl diglycerides due to the reduction of ester groups.

4. Other deuterium-labelled hydrophilic synthons of lipid molecules

Deuterium-labelled [²H₂]-serine is commercially available and can be used in enzymic or chemical syntheses of deuterium-labelled

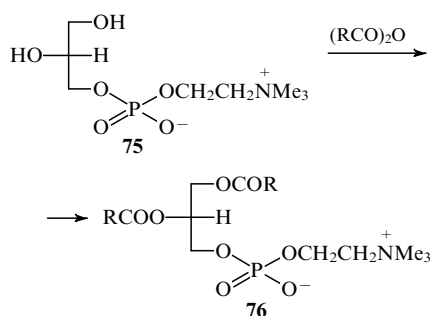
phosphatidylserines. A synthesis of L-serine stereospecifically labelled with deuterium from labelled asparagine has been described.⁹⁵ A number of publications have been dedicated to the synthesis of glycolipids with deuterium labels in the carbohydrate part.^{92,96–103} Usually, deuteration of carbohydrate fragments is carried out by catalytic exchange in the presence of Raney nickel in D₂O, which results in the exchange of protons geminal to the hydroxyl groups of primary and secondary alcohols.⁹⁶ Glucopyranosides subjected to such exchange accept deuterium labels at positions 2, 3, 4, 6, and 6'. The rate of exchange depends on steric factors and differs markedly for different positions in the carbohydrate moiety. The progress of the proton–deuterium exchange is monitored by ¹³C NMR spectroscopy. In case of glycosyldiglycerides,⁹⁸ dialkyl diglycosyldiglycerides,⁹⁹ and other glycolipids¹⁰¹ devoid of ester groups, the exchange is carried out directly in the glycolipids, which do not undergo destruction. In case of diacyl glycosyldiglycerides, the presence of relatively labile ester bonds precludes the application of this approach. Therefore, deuterium is first incorporated into the carbohydrate fragments, which are further bound to diglycerides by traditional chemical methods.⁹⁷ Deuterium can be incorporated into carbohydrates by reduction with metal deuterides.¹⁰³

IV. Synthesis of phospholipids with deuterated fatty acids

The synthesis of phospholipids with deuterated fatty acids is carried out by traditional methods of lipid chemistry. The synthetic procedures for obtaining phospholipids have been described in manuals,^{69,104} monographs,^{104–106} and reviews.^{107,108} As a rule, original papers dealing with the synthesis and applications of deuterium-labelled phospholipids do not contain the description of experimental techniques, and only references to publications dedicated to the synthesis of non-labelled lipids are given. The experimental procedures that are most commonly employed in lipid chemistry are summarised and reviewed in monographs.^{105,106}

The relatively high cost of deuterium-labelled fatty acids accounts for their incorporation into phospholipid molecules at final stages of the synthesis. The general chemical approaches that are most widely employed for the solution of this task are presented below.

The starting material for the phosphatidylcholine synthesis is *sn*-glycerophosphocholine (**75**) and/or its cadmium adduct. The former is easily prepared by alkaline hydrolysis of natural phosphatidylcholines [most commonly, egg phosphatidylcholine (lecithin)],^{106–108} and is devoid of functional groups that need protection in the acylation. By selecting the deuterium-labelled fatty acids, one can synthesise the desired phosphatidylcholine **6** in one step (Scheme 4):



The acylation is performed with acid chlorides,¹⁰⁷ anhydrides,^{109–112} imidazolides,¹¹³ or other activated derivatives of fatty acids.¹⁰⁴ The acylation of *sn*-glycerophosphocholine **75** can be accompanied by the formation of large amounts of side products, mostly, cyclic phosphate. Therefore, this reaction requires that the preselected experimental conditions were strictly met. Then the

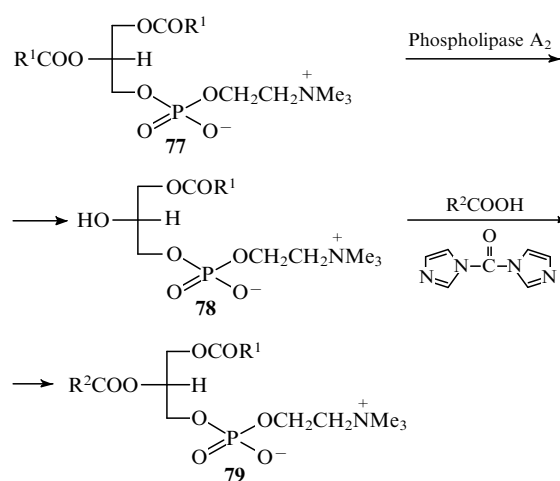
yields at the stage of acylation of *sn*-glycerophosphocholine **75** reach 60%–80% irrespective of the acylating agent used.

The most convenient in the experimental sense are the methods of acylation of *sn*-glycerophosphocholine deuterium-labelled fatty acid with anhydrides and imidazolides. In earlier studies, fatty acid salts have been used as the catalysts for acylation with acid anhydrides;¹¹¹ later, these were replaced by 4-*N,N*-dimethylaminopyridine,¹⁰⁸ sodium methylsulphenylmethanide,¹⁰⁹ and 4-pyrrolidinopyridine.¹¹⁰ Acylation in these cases occurs under milder conditions and is less time-consuming, which is especially important in the synthesis of unsaturated phosphatidylcholines. Fatty acid anhydrides are prepared by treating fatty acids with dicyclohexylcarbodiimide.

Fatty acid imidazolides are obtained upon interaction of the acid with carbonyldiimidazole.^{105,106,113} The imidazolid method is advisable for the synthesis of phospholipids containing expensive labile labelled fatty acids (including spin-labelled ones),¹¹³ since exhaustive acylation with imidazolides requires lesser amounts of the fatty acid than the anhydride method. After acylation has been completed, the excess of the non-consumed fatty acid can be isolated at the stage of chromatographic purification of phosphatidylcholine.

Let us consider the synthesis of phosphatidylcholines with the use of the anhydride method. As can be seen from Scheme 4, in this case phosphatidylcholine synthesis gives only phosphatidylcholines **76** that contain the same fatty acid residues at positions 1 and 2 of glycerol. This is a serious pitfall of this method, since natural phospholipids contain, as a rule, non-identical fatty acids.

The synthesis of these phospholipids rests on the use of lysophosphatidylcholine **78** as the starting compound, which can be easily obtained by enzymic hydrolysis of phosphatidylcholine **77** with phospholipase A₂.^{104,108,114}



Scheme 4

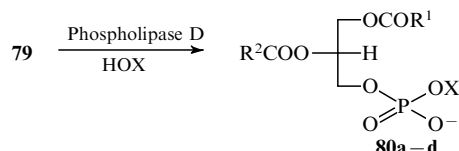
The hydrolysis of phosphatidylcholines does not necessarily require purified preparations of phospholipase A₂. They can be successfully replaced by whole snake or bee venoms. The hydrolysis of phosphatidylcholine with phospholipase A₂ occurs with a high degree of stereoselectivity and can be used for separation of racemic mixtures of synthetic phospholipids.^{104,108,114} The acylation of lysophosphatidylcholines is carried out by the same methods as that of *sn*-glycerophosphocholine, *e.g.*, with a fatty acid imidazolid. By combining various fatty acids in the synthesis of phosphatidylcholines **77** and **79**, one can obtain phosphatidylcholine **79** with any desired set of fatty acid residues including isotopically labelled fatty acids.

These methods of phosphatidylcholine synthesis by acylation of glycerophosphate derivatives have turned out to be very convenient in the preparative sense and they have nearly ousted total chemical synthesis, at least in the case of diacylphosphatidylcholines. The acylation of barium *sn*-glycerophosphate has also been successfully used in the synthesis of perdeuterated

phosphatidic acid, which was further used to obtain perdeuterated phosphatidylcholine.⁷³

However, the synthesis of other phosphoglycerides by acylation of glycerophosphate derivatives is a far more complex problem. Synthesis of such phospholipids as phosphatidylethanolamine, -glycerol, -inositol, and -serine requires that all the functional groups that can be acylated (with the exception of the hydroxy groups of glycerol) be selectively protected and the protecting groups removed in subsequent stages with the preservation of the structure of the synthetic glycerophospholipids. This is rather difficult to accomplish, which is the reason for the low yields of the target product.

A way to overcome this problem is the extensive use of a combination of chemical and enzymic methods and available phosphatidylcholines as the starting material. The phosphatidylcholines **79** with any desired set of fatty acids can be obtained by the above methods and further converted into other glycerophospholipids **80** by the transphosphatidyltransfer reaction catalysed by phospholipase D.^{104–106, 114} A prerequisite for this reaction is a large excess of the alcoholic component (glycerol, ethanolamine, serine, inositol), to which the phosphatidyl group is transferred. The yields of the glycerophospholipids **80a–d** make up to 80%. The only side product of this reaction is phosphatidic acid **80a**. It is impossible to avoid the formation of phosphatidic acid, since this enzymic reaction is carried out in aqueous media, and water competes with an alcohol for the binding with the phosphatidyl residue.



X = H (**a**); $\text{CH}_2\text{CH}_2\text{NH}_3^+$ (**b**); $\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$ (**c**);
 $\text{CH}_2\text{CH}(\text{NH}_3^+)\text{COO}^-$ (**d**).

The experimental procedures based on the use of lipolytic enzymes in lipid chemistry have been considered in detail in some monographs.^{105, 106, 114}

A simple one-step procedure of deuterium incorporation into fatty acid residues of phospholipids is based on the catalytic reduction of double bonds of unsaturated phospholipids.^{115, 116} However, this approach has not found wide use in the synthesis of deuterium-labelled phospholipids, since the reduction of double bonds results in saturated phospholipids the labelled methylene groups of which contain only one deuterium atom. To ensure identical sensitivity in further membrane studies, the content of lipids with CHD labels in the samples must be increased twofold in comparison with lipids containing analogous CD₂ labels.

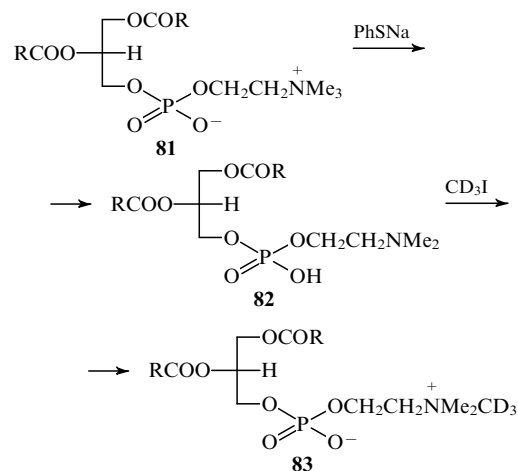
To obtain lipids with deuterium-labelled hydrophobic substituents, total chemical synthesis is employed.¹¹⁷ Normally, this is applied to obtain lipids of non-natural structure. Thus Sunamoto *et al.*¹¹⁷ described the synthesis of 1,2-[8-²H₂]-dimyristoylamino-1,2-dideoxyphosphatidylcholine, a phospholipid in which ester groups have been substituted by amide ones.

V. Synthesis of phospholipids with deuterium labels in the hydrophilic part of the molecule

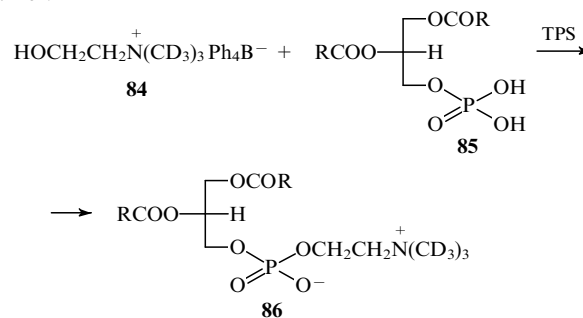
As in the case of phospholipids with labelled fatty acids, the synthesis of phospholipids with deuterium labels in the hydrophilic part of the molecule is carried out by traditional methods of lipid chemistry. At the same time, the introduction of deuterium-labelled hydrophilic groups into lipid molecules has a number of distinctive features.

An original procedure for the introduction of a labelled methyl group into the γ -position of choline has been described by Stoffel *et al.*¹¹⁸ In this method one of the methyl groups of choline is selectively removed upon treatment of the phosphati-

dylcholine **81** with sodium thiophenoxide. The *N,N*-dimethylphosphatidylethanolamine **82** formed was alkylated with trideuteriomethyl iodide to give the phosphatidylcholine **83** with one deuteriomethyl group at the γ -position of choline. It should be borne in mind that alkylation with methyl iodide of amino groups of unsaturated phospholipids can be accompanied by modification of double bonds,¹¹⁹ apparently due to the presence of free iodine in the reaction medium.

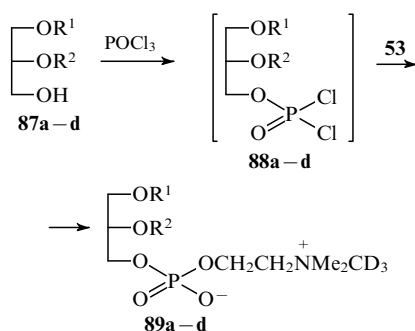


The incorporation of deuterium labels into phospholipids is also carried out at the stage of formation of the phosphodiester bond. The tetraphenylborate of deuterated choline [$\text{HOCH}_2\text{CH}_2\text{N}(\text{CD}_3)_3\text{BPh}_4^-$, **84**], which is soluble in organic solvents, is phosphorylated with phosphatidic acid **85** in the presence of 2,4,6-triisopropylbenzenesulfonyl chloride as the condensation agent.⁷⁴ The reaction is carried out in pyridine. The yield of phosphatidylcholine **86** is 70%. Reactions with other deuterated cholines, **40** and **50**, occur analogously. Phosphatidic acid **85** is an accessible phospholipid, which can be obtained by phosphorylation of the corresponding diglycerides with phosphorus oxychloride^{79, 120} followed by hydrolysis of phosphodichlorides or by enzymic hydrolysis of phosphatidylcholines with phospholipase D.¹¹⁴ Choline tetraphenylborates with different deuterium labels are obtained according to the schemes described earlier.⁷⁴



R = $(\text{CH}_2)_{12}\text{Me}$; TPS = 2,4,6- $\text{Pr}_3\text{C}_6\text{H}_2\text{SO}_2\text{Cl}$.

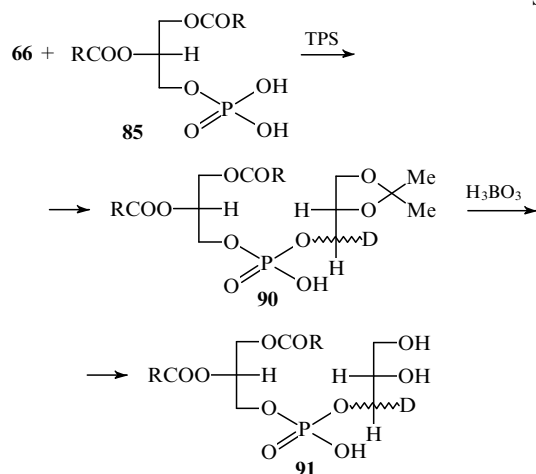
Phospholipids of a particular structure or phospholipids having several different deuterium labels are obtained by using procedures based on total chemical synthesis. Chudinov *et al.*²⁴ described the synthesis of a series of diacyl, dialkyl, alkylacyl, and acylalkyl phosphatidylcholines **89a–d**. The synthesis of phosphatidylcholines **89a–d** involved the total chemical synthesis of the deuterium-labelled diglycerides **87a–d** and their subsequent phosphorylation with phosphorus oxychloride; the phosphodichlorides **88a–d** formed in this reaction were directly (without isolation) brought into the reaction with choline tosylate **53** using the method described by Brockerhoff and Ayengar.⁷⁹ The yield of the product at the stage of phosphorylation was 70%–80%.



$R^1 = \text{COCD}_2(\text{CH}_2)_{13}\text{Me}$, $R^2 = \text{CO}(\text{CH}_2)_{14}\text{Me}$ (a);
 $R^1 = \text{CH}_2\text{CD}_2(\text{CH}_2)_{13}\text{Me}$, $R^2 = \text{CO}(\text{CH}_2)_{14}\text{Me}$ (b);
 $R^1 = \text{CD}_2(\text{CH}_2)_{14}\text{Me}$, $R^2 = (\text{CH}_2)_{15}\text{Me}$ (c);
 $R^1 = \text{COCD}_2(\text{CH}_2)_{13}\text{Me}$, $R^2 = (\text{CH}_2)_{15}\text{Me}$ (d).

The chemical synthesis of deuterium-labelled phosphatidylglycerols **91** has been described.^{87,89} The deuterium-labelled glycerol **66** in which two hydroxy groups were blocked by isopropylidene protection was phosphorylated with phosphatidic acid **85** in the presence of a condensation agent. At the last stage, the isopropylidene protecting group in the compound **90** was removed by relatively mild treatment with boric acid. Depending on the structure of the isopropylidene glycerol used for phosphorylation, one can obtain phosphatidylglycerols with labels at any position in glycerol and of any desired stereoconfiguration. However, the yield of phosphatidylglycerols is rather low (30%) (Scheme 5).

Scheme 5



Yet another method for the introduction of deuterium-labelled glycerol into phosphatidylglycerols is based on the use of the transphosphatidyl transfer reaction catalysed by phospholipase D, much as is the case of the compound **80**. The transphosphatidyl transfer is also used to obtain other glycerophospholipids. It should be noted that this reaction requires a large excess of the alcoholic component. Thus in the synthesis of 1,2-dipalmitoyl-*sn*-glycero-3-phospho-[1,1-²H₂]-ethanolamine and 1,2-dipalmitoyl-*sn*-glycero-3-phospho-[2,2-²H₂]-ethanolamine, a 100-fold excess of the appropriate deuterium-labelled ethanolamine relative to 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine was used.⁸³

VI. Synthesis of fully deuterated lipids

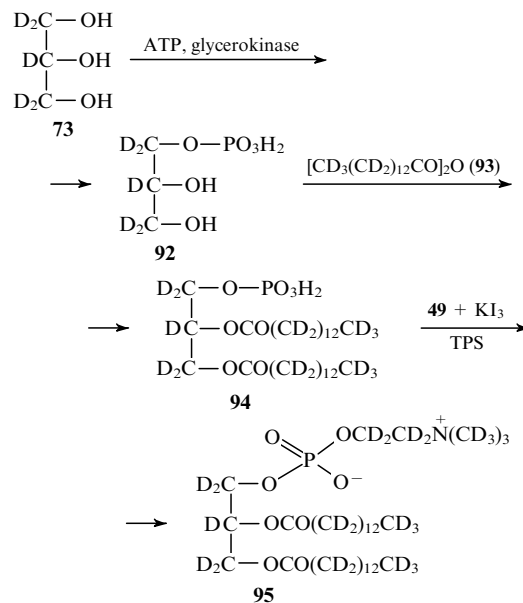
It has already been mentioned that perdeuterated lipids can be used as a transparent matrix for structural analyses of membrane proteins by high-resolution two-dimensional ¹H NMR. This has predetermined the interest in the synthesis of these compounds. There is only one publication in the literature that is dedicated to the synthesis of perdeuterated phospholipids.⁷³

1. Synthesis of perdeuterated phosphatidylcholine

The synthesis of perdeuterated 1,2-dimyristoyl-*sn*-glycero-phosphocholine (**95**) was carried out according to Scheme 6.⁷³ Perdeuterated glycerol **73** was obtained by the reduction of diethyl oxomalonate **72** with lithium aluminium deuteride. In order to obtain the desired stereoconfiguration of the substituted glycerol, an original approach has been developed, which was based on the phosphorylation of free glycerol with ATP in the presence of glycerokinase. This reaction results in high yield (66%) of glycerophosphate **92** with the same stereoconfiguration as that of the natural glycerophospholipids. Glycerophosphate **92** was isolated by precipitation from an aqueous solution as the barium salt, further converted into the pyridinium salt by ion-exchange chromatography, and then acylated with a perdeuterated myristic anhydride (**93**) in pyridine in the presence of 4-*N,N*-dimethylaminopyridine. The yield of 1,2-dimyristoyl-*sn*-glycero-3-phosphate (**94**) exceeded 90%. Perdeuterated myristic acid was obtained by the exchange on a platinum catalyst (similar to the compound **10**) and converted into the anhydride with dicyclohexylcarbodiimide. Phosphatidic acid **94** was condensed with perdeuterated choline in the presence of 2,4,6-triisopropylbenzenesulfonyl chloride. To increase the solubility of choline in organic solvents, choline iodide **49** was converted into a complex with iodine by interaction with KI₃. The yield at the stage of the phosphorylation of choline with phosphatidic acid reaches 25%–40%.⁷³

The use of choline tetraphenylborate permits an increase in the yield of the phosphatidylcholine **95** up to 70%.⁷⁴

Scheme 6



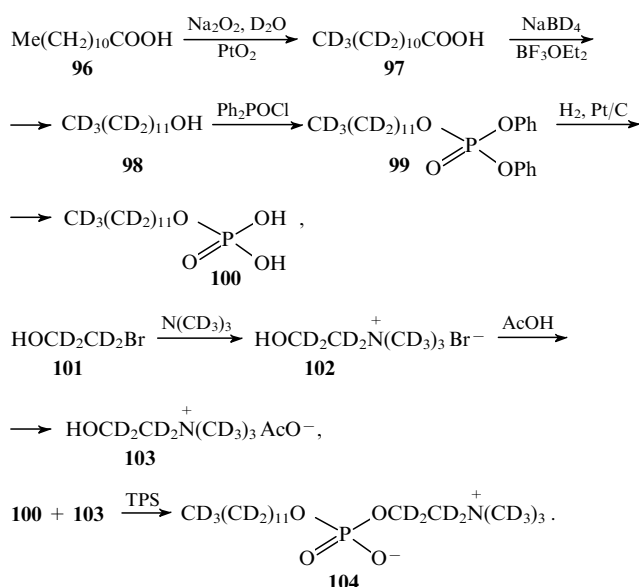
2. Synthesis of perdeuterated phospholipid-like detergents

In studies of secondary and tertiary structures of proteins in the membrane environment by two-dimensional ¹H NMR spectroscopy, perdeuterated sodium dodecyl sulfate is mostly used. The use of perdeuterated sodium dodecyl sulfate in these studies is motivated by its commercial availability. Meanwhile, sodium dodecyl sulfate is not a close structural analogue of natural phospholipids. A search for more close structural analogues of phospholipids has stimulated studies aimed at the synthesis of novel detergents.

It was proposed to use dodecyl phosphocholine as a phosphatidylcholine analogue. The structure of its polar region fully corresponds to that of phosphatidylcholine. At the same time, the presence of only one short-chain hydrocarbon residue accounts for the fact that dodecyl phosphocholine forms micelles in water. The critical micelle concentration is 1.1 mmol litre⁻¹,¹²¹ the micelle diameter is about 50 Å, and one micelle comprises 56±5 molecules of dodecyl phosphocholine.¹²²

Dodecyl phosphocholine has been used in membrane studies for simulating the interaction between phospholipase A₂ and the lipid bilayer surface.¹²¹ The synthesis of non-deuterated dodecyl phosphocholine involved the phosphorylation of dodecyl alcohol with 2-bromoethyl phosphodichloride and subsequent reaction of the bromoalkyl derivative with trimethylamine.¹²¹ The first total chemical synthesis of perdeuterated dodecyl phosphocholine (**104**) was carried out in 1979.⁷⁷ The starting compound was lauric acid (**96**), which was subjected to total proton–deuterium exchange by the previously described method.²⁷ Perdeuterated lauric acid (**97**) was reduced to the alcohol (**98**). Perdeuterated dodecanol **98** was phosphorylated with diphenylphosphinoyl chloride. The protecting phenyl groups in the compound **99** were removed by catalytic hydrogenolysis to give dodecyl phosphate (**100**).

The choline component was obtained by quaternisation of perdeuterated trimethylamine with 2-bromoethanol (**101**); the resulting choline bromide (**102**) is converted into the acetate (**103**) in order to increase its solubility in organic solvents. Choline acetate **103** is phosphorylated with the phosphate **100** in the presence of 2,4,6-triisopropylbenzenesulfonyl chloride to give perdeuterated dodecyl phosphocholine (**104**).

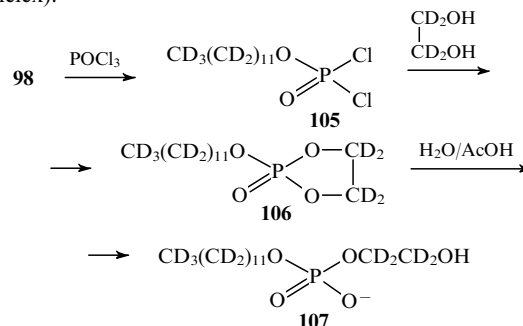


This scheme is multistep; the procedure of synthesis of perdeuterated choline was later modified.

Thus Dekker *et al.*¹²³ reduced perdeuterated lauric acid **97** with lithium aluminium deuteride to give the alcohol **98**, which was further phosphorylated with phosphorus oxychloride. The resulting phosphodichloride [CD₃(CD₂)₁₁OP(O)Cl₂, **105**] was hydrolysed with aqueous hydrochloric acid and dodecyl phosphate **100** was precipitated with acetone. Perdeuterated choline in the form of tetraphenylborate **40** was condensed with dodecyl phosphate in the presence of 2,4,6-triisopropylbenzenesulfonyl chloride. The isolation of dodecyl phosphocholine (**104**) was associated with certain difficulties due to its good solubility in water, which excludes extraction. Perdeuterated dodecyl phosphocholine **104** is now commercially available.

Another representative of phospholipid-like detergents is dodecyl phosphoethylene glycol. It represents a structural analogue of the negatively charged phospholipid, phosphatidylglycerol. Together with dodecyl phosphocholine, perdeuterated dodecyl phosphoethylene glycol (**107**) was used to study the effect of lipid environment on the secondary structure of a mitochondrial signal peptide by high-resolution two-dimensional ¹H NMR spectroscopy.¹²⁴ The synthesis of perdeuterated dodecyl phosphoethylene glycol was carried out as described earlier.¹²⁵ Dodecanol **98** was phosphorylated with phosphorus oxychloride and the phosphodichloride (**105**) then reacted with perdeuterated ethylene

glycol to give phospholane **106**. The latter was hydrolysed in the presence of acetic acid to give dodecyl phosphoethylene glycol **107**. All these reactions proceeded in high yields; intermediate products were not isolated. It is necessary to note that dodecyl phosphoethylene glycol possesses chelating properties and after conventional purification procedures it may contain polyvalent cations. It is therefore recommended to convert it into the sodium salt using ion-exchange resins containing chelating groups (*e.g.*, Chelex).¹²⁶



VII. Other deuterium-labelled lipids

In addition to phospholipids, biological membranes of eukaryotic cells contain cholesterol, the content of which can make up to 25% of the total pool of membrane lipids.¹²⁷ Cholesterol plays an important role in the regulation of the phase state of the lipid bilayer.¹²⁸ To study its interaction with phospholipids by the ²H NMR method, cholesterol with deuterium labels at different positions of the molecule and its derivatives have been synthesised.^{129, 130} Syntheses of deuterium-labelled sterols are performed by methods analogous to those used in the synthesis of deuterium-labelled fatty acids.

In some cases, when chemical synthesis of deuterium-labelled lipids is a rather difficult task, microbiological synthesis can be applied. This is exemplified by the synthesis of deuterium-labelled plasmalogens.¹³¹ The incorporation of specifically deuterated glycerols into cardiolipin is achieved by growing *E. coli* cells on culture media containing deuterium-labelled glycerol.^{89, 90, 132, 133}

An analogous approach was used to incorporate deuterium-labelled oleic acid into cardiolipin and phosphatidylglycerol¹³⁴ as well as of deuterium-labelled palmitic acid into the *E. coli* membrane.¹³⁵ To this end, *E. coli* cells were grown on a culture medium containing the fatty acid and a detergent. Depending on the problem to be solved, different strains of *E. coli* were used.^{89, 90, 132–135} Lipids were isolated from the culture mass by conventional methods, which included cell disintegration, extraction, and chromatographic purification. The resulting phospholipid preparations represented mixtures of homologues differing in the length and degree of unsaturation of hydrocarbon residues.

Deuterium-labelled fatty acids that are used as a nutrition source for bacteria can be involved in the biosynthesis of other fatty acids, being converted into other deuterium-labelled acids.^{134, 136} Microbiological synthesis can be used for obtaining perdeuterated lipids. The synthesis of perdeuterated fatty acids by culturing of *Scenedesmus obliquus* cells on a culture medium containing heavy water has been described.¹³⁷

Deuterium-labelled fatty acids of various structures and having labels at different positions of the hydrocarbon chain were incorporated into the membrane of a mycoplasma *A. laidlawii*, which made possible a detailed profile analysis of the order parameter of hydrocarbon chains.^{138–142}

VIII. Analysis of deuterium-labelled lipids

In the synthesis of deuterium-labelled lipids, it is often necessary to monitor the isotopic purity of intermediate and final products and to establish the selectivity of the label incorporation. These

problems can be solved by mass spectrometry, high resolution NMR, gas-liquid, and liquid chromatography.^{30,31}

Mass spectrometry offers a direct and the most sensitive method of analysis of the content of deuterium in organic compounds. The main information about the use of this method in the study of lipids labelled with stable isotopes is given in the review by Rohwedder.¹⁴³ It is suggested that labelled and non-labelled molecules are ionised to the same degree. The measurements have to be performed under conditions that ensure minimum fragmentation of the molecular ion. Prior to analysis compounds with an enhanced tendency for fragmentation (unsaturated acids and alcohols) are converted into silyl derivatives.^{36,49}

The isotopic purity and the position of deuterium labels in the lipids and the intermediates used in the lipid synthesis can be established by ¹H NMR spectroscopy.^{4–6} This method is used for the elucidation of the structure of intermediates and/or lipids that are synthesised. The position and content of deuterium labels is determined from a decrease in the integral intensity of the signal in ¹H NMR spectra corresponding to protons that are replaced by deuterium. However, many signals in the ¹H NMR spectra of lipids overlap, which affects the accuracy of the analysis.

In principle, these problems can be solved with the help of high-resolution ²H NMR. In contrast to ¹H NMR, ²H NMR spectra contain signals from deuterium labels alone, which significantly simplifies the spectra. However, the range of variations of absolute chemical shifts in the ²H NMR spectra is about 6.5 times more narrow (which is in accord with the gyromagnetic proton-to-deuteron ratio) than in the ¹H NMR spectra. Moreover, in the recording of the ²H NMR spectra one cannot use deuterium stabilisation of the magnetic field of the NMR spectrometer, which also diminishes the resolution. It is therefore rather difficult to differentiate signals from several groups with close chemical shifts despite the relative simplicity of the ²H NMR spectra. To some extent, this problem can be overcome by using shift reagents, which made it possible to resolve deuteron signals in the α -, β -, γ -, and δ -positions of a fatty acid.¹⁴⁴

¹³C NMR spectroscopy is devoid of the shortcomings characteristic of ¹H NMR and ²H NMR. The range of variations of the chemical shifts in the ¹³C NMR spectra is one order of magnitude higher than that in the ¹H NMR spectra and, as a consequence, the majority of signals in the ¹³C-NMR spectra of lipids are resolved. Another advantage of the ¹³C NMR method is that the incorporation of deuterium induces a small isotopic upfield shift of the signal.^{30,31,145} As a result, the spectrum simultaneously manifests resolved signals of carbon atoms covalently bound to deuterons and protons, which increases the accuracy of measurements of the isotopic purity. It should be kept in mind that precise measurements of the ratios of deuterated to non-deuterated products is possible only under conditions when ¹³C NMR spectra are recorded under conditions of complete relaxation and in the absence of the Overhauser effect. The signals of carbon atoms bound to deuterium are readily recognised in the spectra because of the characteristic multiplicity caused by the spin-spin interaction with deuterium. The spin of deuterium $I = 1$, that is the signal of the CD-group is observed as a triplet with lines of equal intensity; the spin-spin coupling constant, J_{CD} , is about 20 Hz. A serious pitfall of the ¹³C NMR method is its low sensitivity, which decreases even more upon substitution of protons for deuterium due to the elimination of the Overhauser effect.

Among other methods of analysis of deuterated fatty acids, special mention should be made of gas-liquid chromatography (GLC). The possibility of separation of deuterium-labelled and non-labelled fatty acids has long been known, but it was difficult to perform.³¹ In the study of Rietveld *et al.*,¹³⁴ GLC was successfully used for the separation of fatty acids as methyl esters, including acids with one deuterium-labelled methylene group.

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Monoterpenoids in the synthesis of optically active insect pheromones

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Abstract. The data on the application of cyclic and acyclic monoterpenoids in the synthesis of optically active insect pheromones are summarised. The bibliography includes 99 references.

I. Introduction

Studies on pheromones have posed many challenging problems to synthetic chemists the solution of which has broadened the range of methods employed in modern organic synthesis. One of these problems is the study of effects of the absolute configuration of chiral molecules on biological activity, since chemical communication in many insect species is mediated by optically active compounds. More than 100 chiral insect pheromones have been identified so far. As the amount of the pheromone produced by each individual species is negligibly small, the accumulation, isolation, and purification of an individual natural substance is a very labourious problem.¹ Therefore, the determination of the absolute configuration of chiral pheromones is based on a stereocontrolled straightforward synthesis of enantiomerically pure compounds rather than on chemical degradation of natural material accessible with difficulty (together with a combination of physicochemical methods). As a rule, the elucidation of the absolute configuration of a natural pheromone requires the synthesis of all of its possible stereoisomers in enantiomerically pure forms and assay of the biological activity of each of them.

Studies of specific responses of insects to each of these possible stereoisomers have demonstrated that the efficiency of attraction of many species increases 2- to 1000-fold if an enantiomer with the absolute configuration of a natural pheromone or a synergistic mixture of enantiomers is used instead of a racemic compound. Obviously, the use of enantiomerically pure or enantiomerically enriched pheromones makes it possible to considerably reduce the

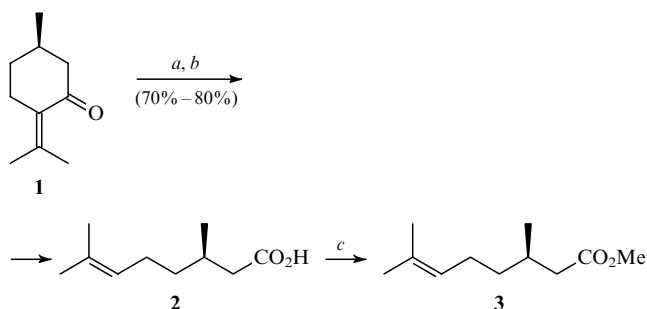
expenditure of materials and the scale of manufacture. However, in order to make the application of these optically active low-molecular-weight bioregulators economically expedient, it is necessary to use the available and inexpensive initial products and simple, practical synthetic schemes.

The currently known chiral insect pheromones are relatively simple molecules (they contain not more than four asymmetric centres and not more than four functional groups). Their structural fragments are sometimes rather peculiar, but the conglomeration of chiral centres and functional groups as in the molecules of carbohydrates, prostanoids, and macrolide antibiotics is not typical of pheromones. Therefore, the 'ideal' chiral building block (CBB) seems to be a moderately functionalised compound devoid of numerous chiral centres. Monoterpenoids, amino acids, and hydroxy acids are the most consistent with this ideal structure. The former are especially suitable for the synthesis of compounds with a branched hydrocarbon skeleton, first of all, of pheromones having an isoprenoid structure. The range of chiral terpenoids is rather wide. All of them are the products of wood-chemical, perfume, food, and pharmaceutical industries.

This review considers the synthetic potentialities of monoterpenoids and the corresponding CBB exemplified in syntheses of optically pure and enantiomerically enriched insect pheromones.

II. Syntheses on the basis of (*R*)-pulegone

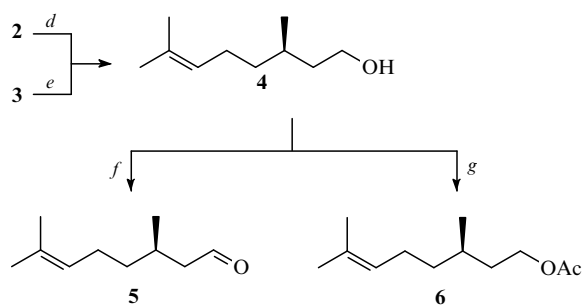
Several chiral building blocks can be synthesised from (*R*)-pulegone **1** by simple transformations. Thus the two-step retrocyclisation of pulegone gives citronellic acid **2**. The latter can be converted into methyl ester **3** and reduced to citronellol **4** with diisobutyl aluminium hydride DIBALH. It can also be obtained directly from the acid **2** by reduction with LiAlH₄. The alcohol **4** is easily converted into citronellal **5** or citronellyl acetate **6**.²



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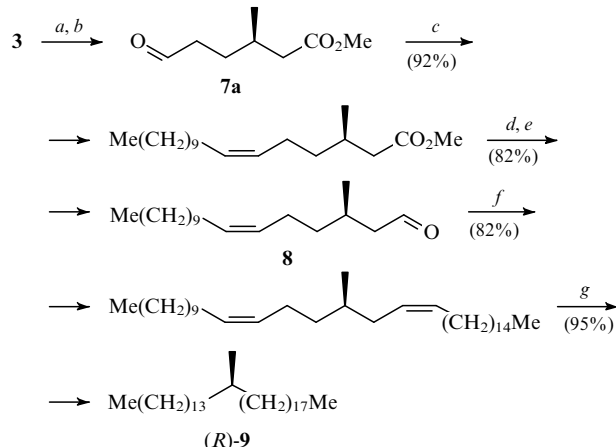
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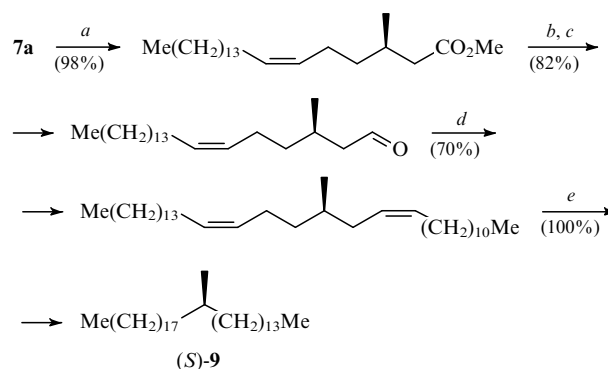
Reagents: (a) HCl; (b) NaOH; (c) MeOH/TsOH; (d) LiAlH₄; (e) Bu₂AlH; (f) Py·CrO₃·HCl (PCC); (g) Ac₂O/Py.

A scheme for the synthesis of the both enantiomers of 15-methyltritriacontane **9**, the pheromone of the stable fly (*Stomoxys calcitrans*), from the oxo ester **7a**, which is the product of ozonolysis and reduction of methyl citronellate **3**, has been proposed.³ The (*R*)-**9** enantiomer was synthesised as follows. At the first stage, the aldehyde ester **7a** reacts with C₁₁-phosphorane; then the reaction product is converted in two steps into the aldehyde **8**, which interacts with another phosphorane to give (*R*)-**9** following hydrogenation.



Reagents: (a) O₃/MeOH; (b) Me₂S; (c) Me(CH₂)₉CH = PPh₃; (d) LiAlH₄; (e) PCC; (f) Me(CH₂)₁₄CH = PPh₃; (g) H₂/Pd/C.

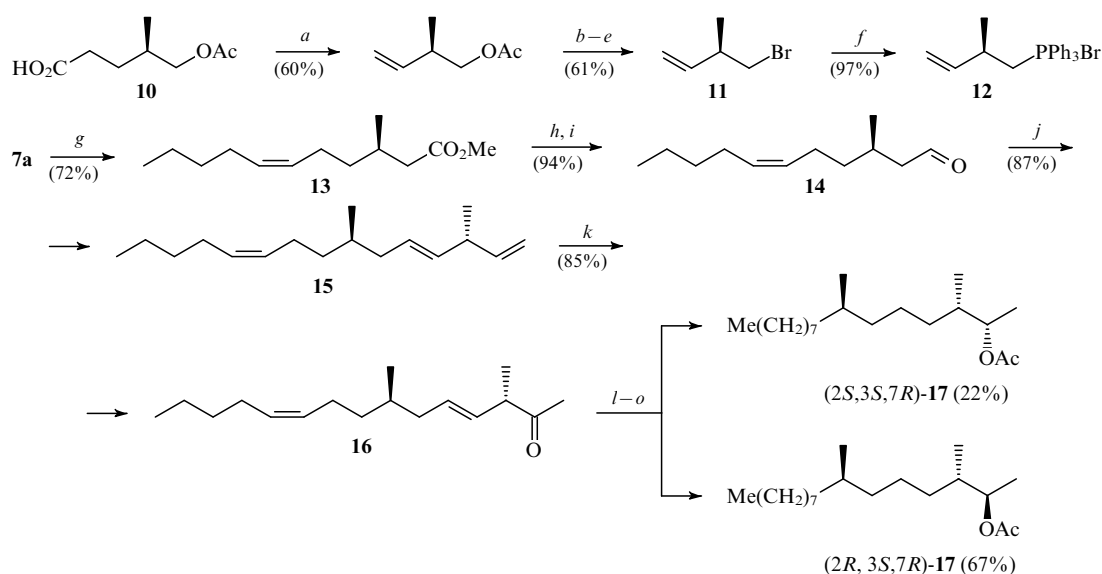
In an analogous scheme of the synthesis of (*S*)-**9**, C₁₅- and C₁₂-triphenylphosphoranes have been employed.³



Reagents: (a) Me(CH₂)₁₃CH = PPh₃; (b) LiAlH₄; (c) PCC; (d) Me(CH₂)₁₀CH = PPh₃; (e) H₂/Pd/C.

Pathways for the synthesis of two diastereomers of 2-acetoxy-3,7-dimethylpentadecane **17**, the analogues of diprionyl acetate, the sex pheromone of the sawflies related to the *Diprion* and *Neodiprion* genera, on the basis of the aldehyde ester **7a** and (4*R*)-methyl-5-acetoxypentanoic acid **10**, have been proposed. The C(7)-chiral centre of the target molecule, which has the (*R*)-configuration, was introduced *via* the building block **7a**. Another CBB, the compound **11**, was used for the creation of the C(3)-chiral centre after its conversion into the phosphonium salt **12**. The chiral C(2)-centre is formed in the reduction of the methyl ketone **16** corresponding to the target structure. Thus, the synthesis of the compound **17** was carried out essentially in two steps. In the first step, the alkenoate **13** obtained by alkenation of **7a** was converted into the aldehyde **14** by a two-step procedure.^{4,5} The second part of this synthesis involves the interaction of the aldehyde **14** with the phosphorane prepared from the salt (*R*)-**12** and subsequent selective transformations of the triene **15**: the oxidation of the terminal double bond and borohydride reduction of the methyl ketone **16** into a mixture of diastereoisomers in which the *threo*-isomer predominates (Scheme 1). They were separated by HPLC.

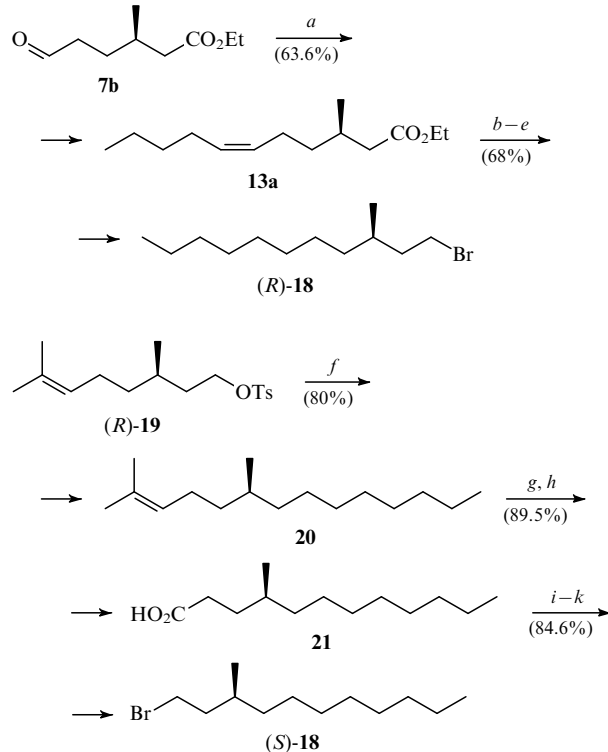
The synthesis of three diastereomers of diprionyl acetate **17** from the aldehyde ester **7b** is based on the coupling of the C₁₂- and C₅-building blocks **18** and **24** of the respective configuration.⁶ The



Scheme 1

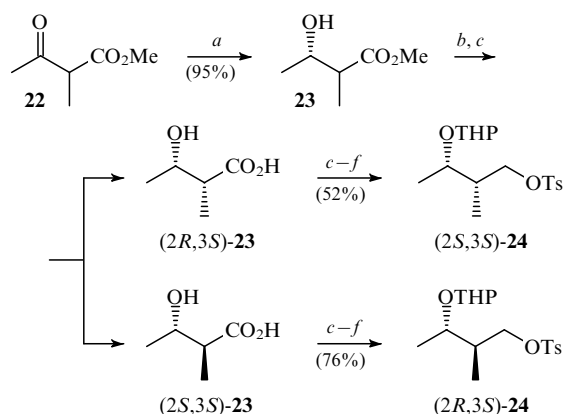
Reagents: (a) Pb(OAc)₄/Cu(OAc)₂·H₂O; (b) KOH; (c) BuⁿLi; (d) TsCl; (e) NaBr; (f) PPh₃/14 kbar; (g) BuCH = PPh₃; (h) Bu₂AlH; (i) PCC; (j) **12**/BuⁿLi; (k) O₂/PdCl₂–CuCl; (l) NaBH₄; (m) H₂/Pt; (n) HPLC; (o) Ac₂O/Et₃N/4-dimethylaminopyridine (DMAP).

key stage in the scheme of synthesis of the C₁₂-block of the (*R*)-configuration is the condensation of the aldehyde **7b** with pentylidenephosphorane resulting in the ester **13a**. Its optical antipode, (*S*)-**18**, was synthesised through alkylation of (*R*)-citronellyl tosylate **19**, the ozonolysis of the resulting alkene **20** into the acid **21**, and its conversion into the bromide by the Hunsdiecker reaction.



Reagents: (a) BuCH=PPh₃; (b) H₂/PtO₂; (c) LiAlH₄; (d) TsCl/Py;
(e) LiBr; (f) Me(CH₂)₅MgCl/CuI; (g) O₃/CH₂Cl₂;
(h) H₂O₂/HCO₂H; (i) NaOH; (j) AgNO₃; (k) Br₂.

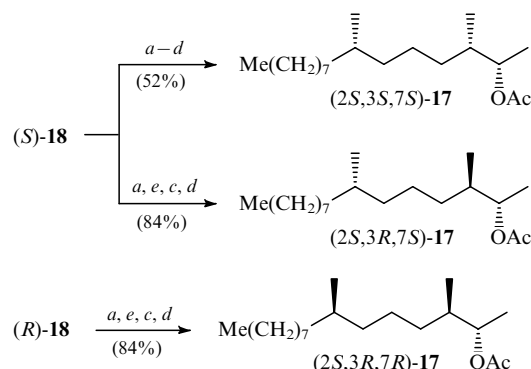
The synthesis of the C₅-blocks **24** having two chiral centres was carried out by diastereoselective asymmetric reduction of methyl 2-methyl-3-oxobutyrates **22** and subsequent fractional crystallisation of first sodium and then ammonium salts. This rather labourious procedure yielded the hydroxy acids (2*R*,3*S*)-**23** and (2*S*,3*S*)-**23**, which were then converted in four steps into the protected diols (2*S*,3*S*)-**24** and (2*R*,3*S*)-**24** required for the synthesis of target products.



Reagents: (a) H₂/Ni-(*S,S*)-[HO₂CCH(OH)]₂; (b) NaOH;
(c) recrystallisation, H₃O⁺; (d) CH₂N₂;
(e) dihydropyran (DHP)/TsOH; (f) LiAlH₄; (g) TsCl/Py.

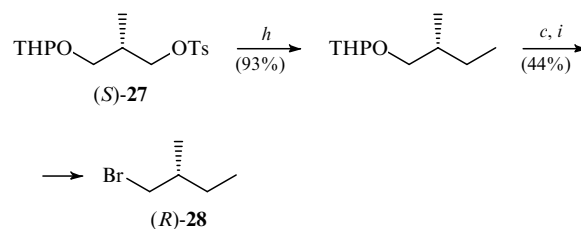
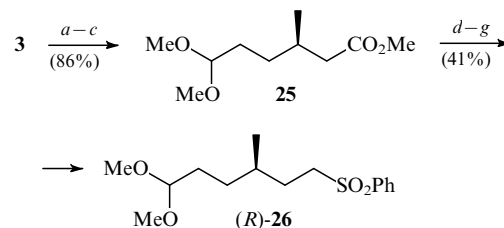
Three optically pure diastereomers of diprionyl acetate **17** were obtained by a Wurtz-type reaction by coupling the stereoisomeric C₅-**24** and C₁₂-**18** blocks (Scheme 2).

Scheme 2



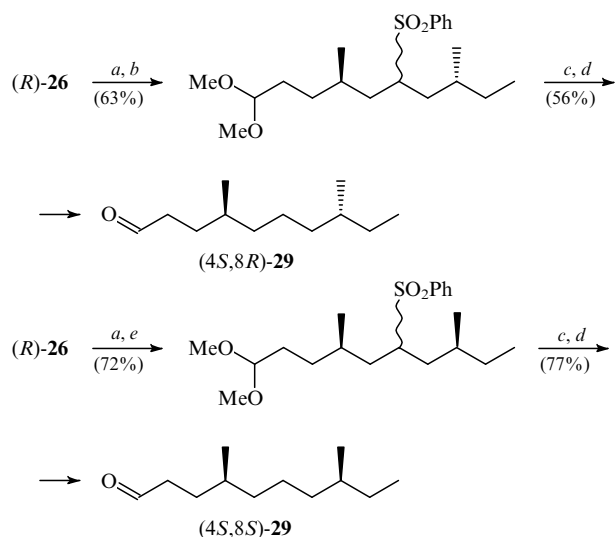
Reagents: (a) Mg; (b) (2*S*,3*S*)-**24**/CuI; (c) TsOH/MeOH; (d) Ac₂O/Py;
(e) (2*R*,3*S*)-**24**/CuI.

Dimethyl acetal **25**, another product of ozonolysis and reduction of methyl citronellate **3**, was used in the synthesis of (4*S*,8*R*)- and (4*S*,8*S*)-4,8-dimethyldecanals **29** manifesting attractant activity against *Tribolium confusum* and *T. castaneum* meal worms. The starting acetal **25** was converted by conventional procedures into the sulfone **26** required for the formation of the (4*S*)-chiral centre of the pheromone **29**. The corresponding enantiomeric, selectively protected diols **27** were converted into bromides **28** and used for the introduction of (8*R*)- and (8*S*)-chiral centres.⁷



Reagents: (a) O₃/MeOH; (b) Me₂S; (c) TsOH, MeOH; (d) LiAlH₄;
(e) TsCl/Py; (f) NaI/NaHCO₃; (g) PhSO₂Na;
(h) MeMgI/Li₂CuCl₄; (i) TsOH/MeOH; (j) Br₂/PPh₃.

The alkylation of the sulfone (*R*)-**26** with the bromides (*R*)-**28** or (*S*)-**28** followed by desulfonation of the condensation products and hydrolysis yields the (4*S*,8*R*)- and (4*S*,8*S*)-stereoisomers of the compound **29**, respectively.



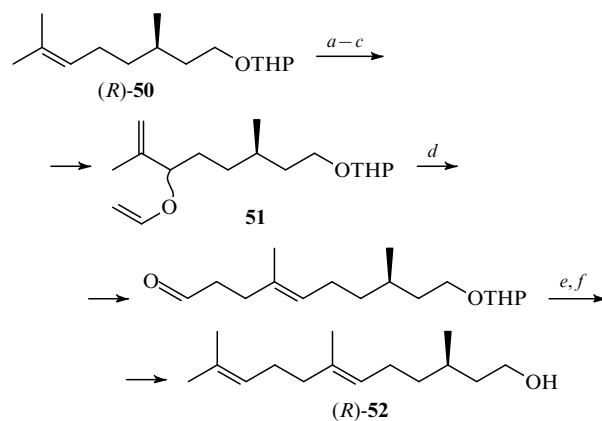
Reagents: (a) Bu^nLi ; (b) $(R)\text{-}28$; (c) Na-Hg ; (d) H_3O^+ ; (e) $(S)\text{-}28$.

The allylic alcohol **30**, the product of the Sharpless oxidation⁸ of the compound **3**, was used as the starting material in the synthesis of both enantiomers of $(5E)$ -isopropyl-3,9-dimethyl-deca-5,8-dienyl acetate **39** the (S) -isomer of which is the sex pheromone of the yellow scale (*Aonidiella citrina*).⁹ The building block $(S)\text{-}32$ obtained from the methyl ester **30** via the acetal **31** was used for the creation of the $(3R)$ -centre in the molecule of **39**. Its optical antipode, the aldehyde $(R)\text{-}32$, was obtained from the same allylic alcohol **30** by converting it into a mixture of mono- and di-ethers (**34** and **35**, respectively) via the diol **33**. The ozonolysis and reduction of this mixture gave the monosubstituted diol **36**, which was converted via the benzyl derivative into another key aldehyde ester, $(R)\text{-}32$. Further transformations of (S) - and $(R)\text{-}32$ involved the condensation with the Grignard reagent **40** and a 2,3-sigmatropic rearrangement of the resulting allylic alcohols **37** into the E -homoallylic alcohols **38** via their stannyl derivatives (Scheme 3). The alcohols **38** were further

converted into the corresponding aldehydes; their alkenation gave the target products, (S) - or $(R)\text{-}39$. The synthesis of the biologically active (S) -enantiomer **39** is shown in Scheme 3.

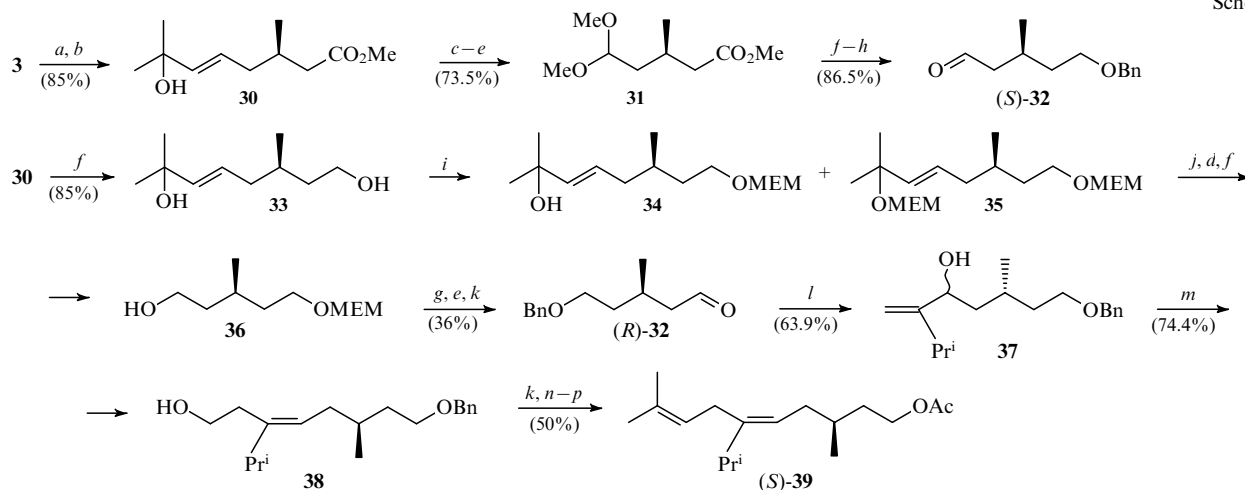
A scheme of synthesis of α -multistriatine **49**, the aggregation pheromone of the elm bark beetle (*Scolytus multistriatus*), on the basis of citronellol **4** has been developed. Thus, pyrolysis of the xanthate **41** gave the diene $(R)\text{-}42$, which was further converted into the diol **43** by chemospecific epoxidation of the trisubstituted double bond with subsequent hydrolysis of the intermediate epoxide. The oxidative cleavage of **43** gave the aldehyde $(R)\text{-}44$. Its α -methylation was carried out via the intermediate Schiff's base **45**. The resulting aldehyde **46** was converted via the ketone **47** into the epoxide **48**; its treatment with SnCl_4 gave a mixture of four stereoisomers from which **49** was isolated chromatographically (Scheme 4).¹⁰

The tetrahydroxypranylic ether of (R) -citronellol **2**, $(R)\text{-}50$, has proved to be a convenient starting material in the synthesis of $(R)\text{-}(+)\text{-}2,3$ -dihydrofarnesol $(R)\text{-}52$, the antipode of terrestrol, the marker pheromone of the male bumblebee *Bombus terrestris*. To this end, $(R)\text{-}50$ was converted into a mixture of the diastereo-



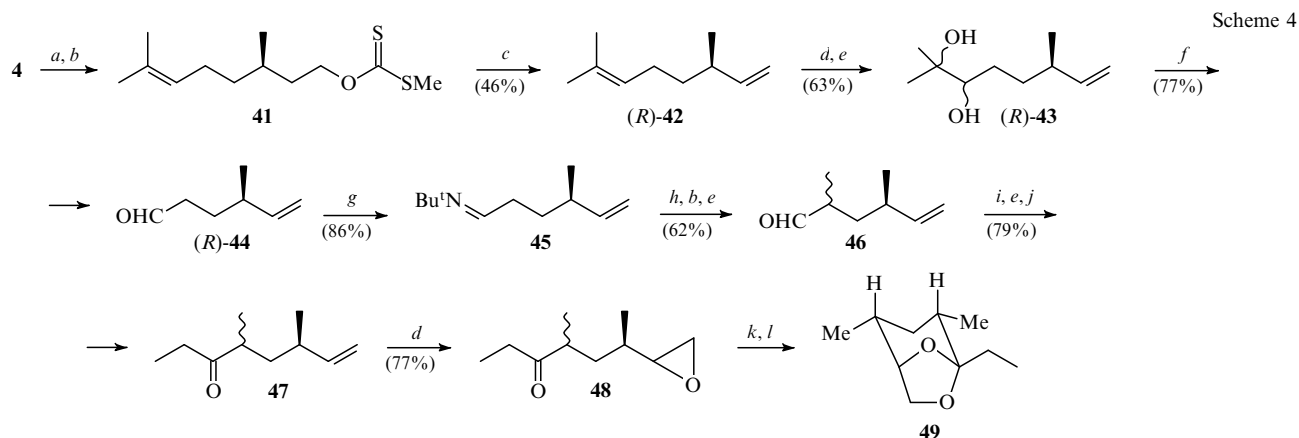
Reagents: (a) MCPBA; (b) LDA; (c) $\text{OEt}/\text{Hg}^{2+}$; (d) 180°C ; (e) $\text{Ph}_3\text{P}=\text{CMe}_2$; (f) H_3O^+ .

Scheme 3



Reagents: (a) $\text{Ph}_2\text{Se}_2/\text{H}_2\text{O}_2$; (b) Bu^tOOH ; (c) O_3/MeOH ; (d) Me_2S ; (e) MeOH/TsOH ; (f) LiAlH_4 ; (g) $\text{PhCH}_2\text{Br}/\text{NaH}$; (h) HClO_4 ; (i) $\text{MEM}-\text{Cl}/\text{NaH}$ [$\text{MEM} = \text{CH}_2\text{O}(\text{CH}_2)_2\text{OMe}$]; (j) $\text{O}_3/\text{MeOH}-\text{CH}_2\text{Cl}_2/\text{NaHCO}_3$; (k) $\text{Py} \cdot \text{CrO}_3$;

(l) $\text{C}(\text{Pr}^i)=\text{CH}-\text{MgBr}$ (**40**); (m) (1) $\text{Bu}_3\text{SnCH}_2\text{I}/\text{KH}$; (2) Bu^nLi ; (n) $\text{Me}_2\text{C}=\text{PPh}_3$; (o) Li/NH_3 ; (p) $\text{Ac}_2\text{O}/\text{Py}$.

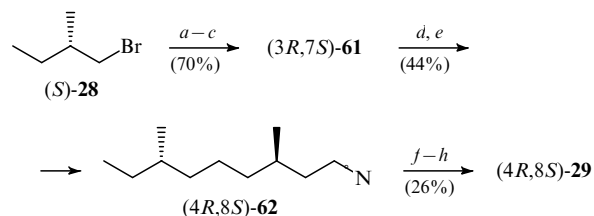


Reagents: (a) CS_2/NaH ; (b) MeI ; (c) 240°C ; (d) $m\text{-ClC}_6\text{H}_4\text{COOOH}$ (MCPBA); (e) H_3O^+ ; (f) $\text{Pb}(\text{OAc})_4$; (g) Bu^tNH_2 ; (h) LDA ; (i) EtMgBr ; (j) H_2CrO_4 ; (k) SnCl_4 ; (l) HPLC .

meric allyl vinyl ethers **51**. The subsequent Claisen rearrangement and the Wittig alkenation of the intermediate aldehyde gave (R)-**52**.¹¹

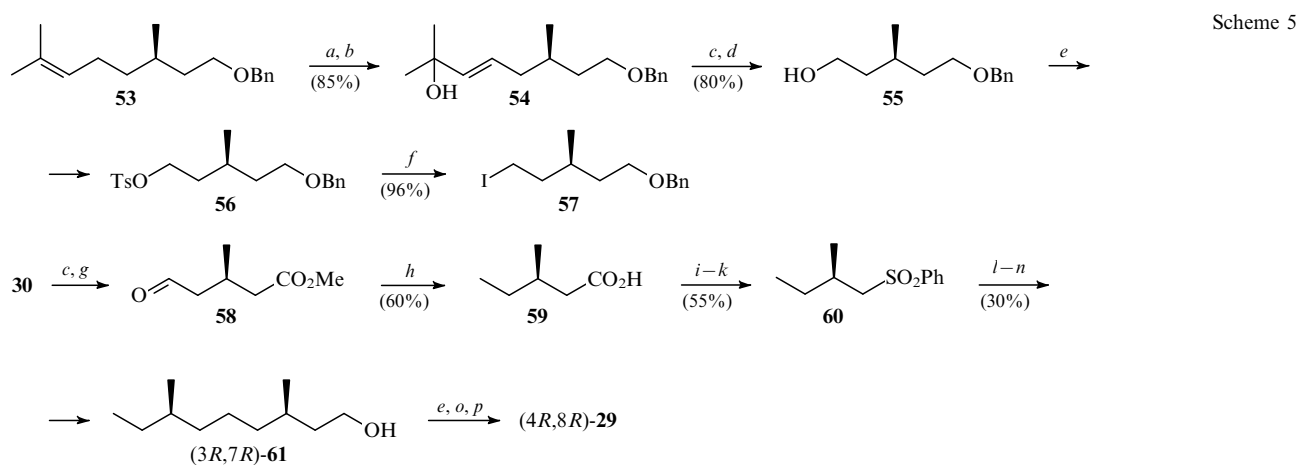
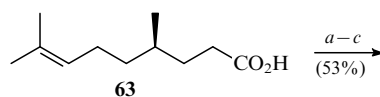
The derivatives of citronellol **4** have been used to obtain all the stereoisomeric 4,8-dimethyldecanals **29**.¹² In the synthesis of (4*R*,8*R*)-**29** and (4*R*,8*S*)-**29**, the original benzyl ether **53** underwent the Sharpless oxidation⁸ into the allylic alcohol **54**. Ozonolysis of the latter and reduction gave the monoprotected diol **55**. Its derivatives, the tosylate **56** and the iodide **57**, have found application in the formation of the (4*R*)-chiral centre of **29**. The sulfone **60**, which has been prepared in several steps including the ozonolysis of the compound **30** into the aldehyde ester **58** and Huang–Minlon reduction of the latter into the acid **59**, was used for the formation of the (8*R*)-centre. The reaction of **60** with the iodide **57** and subsequent desulfonation of the condensation product yielded the alcohol (3*R*,7*R*)-**61**; its homologisation into the target aldehyde (4*R*,8*R*)-**29** was performed *via* the corresponding cyanide (Scheme 5).

For the formation of the (8*S*)-centre in the stereoisomer (4*R*,8*S*)-**29**, (2*S*)-methylbutyl bromide **28** has been used. Its reaction with the tosylate **56** gave the alcohol (3*R*,7*S*)-**61**, which was converted into the target product *via* the nitrile (4*R*,8*S*)-**62**.

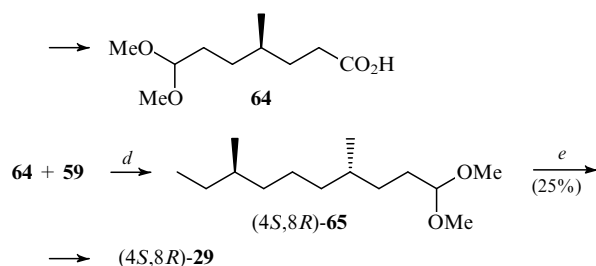


Reagents: (a) Mg ; (b) **56**/ Li_2CuCl_4 ; (c) $\text{H}_2/\text{Pd/C}$; (d) TsCl/Py ; (e) NaCN ; (f) NaOH ; (g) LiAlH_4 ; (h) PCC .

Electrolysis of a mixture of the acids **59** and **64** (obtained by ozonolysis of homocitronellic acid **63**) in MeONa/MeOH gave a mixture of the corresponding hydrocarbon, bisacetal, and (4*S*,8*R*)-**65**; the latter was isolated chromatographically. Compound (4*S*,8*R*)-**29** was obtained by treatment of (4*S*,8*R*)-**65** with HClO_4 .

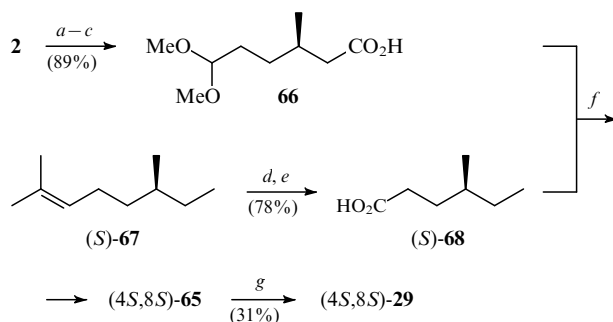


Reagents: (a) $\text{Ph}_2\text{Se}_2/\text{H}_2\text{O}_2$; (b) Bu^tOOH ; (c) $\text{O}_3/\text{CH}_2\text{Cl}_2 - \text{MeOH/NaHCO}_3$; (d) NaBH_4 ; (e) TsCl/Py ; (f) NaI ; (g) Me_2S ; (h) $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O/KOH}$; (i) $\text{Pb}(\text{OAc})_4/\text{I}_2$; (j) PhSNa ; (k) MCPBA ; (l) Bu^nLi ; (m) **57**; (n) Li/EtNH_2 ; (o) NaCN ; (p) Bu_2^iAlH .



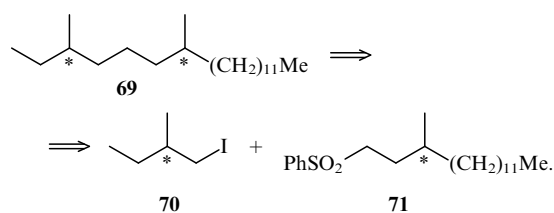
Reagents: (a) O_3/MeOH ; (b) Me_2S ; (c) MeOH/TsOH ;
 (d) e^- , NaOMe/MeOH ; (e) HClO_4 .

The synthesis of the (*S,S*)-enantiomer **29** is based on the same principle. In this case, the role of chiral building blocks was played by the acids **66** and (*S*)-**68** synthesised from the products of ozonolysis of the acid **2** and tetrahydromyrcene (*S*)-**67**, respectively. The acetal (*4S,8S*)-**65** obtained in the electrolysis of an equimolar mixture of the acids **66** and (*S*)-**68** was further converted into the target product, (*4S,8S*)-**29**.

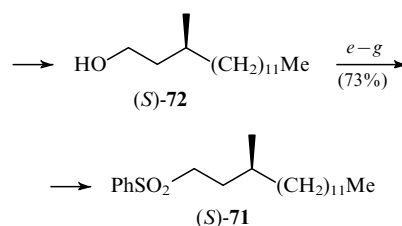
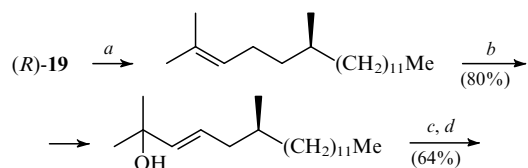


Reagents: (a) O_3/MeOH ; (b) Me_2S ; (c) MeOH/TsOH ; (d) $\text{O}_3/\text{Me}_2\text{CO}$;
 (e) H_2CrO_4 ; (f) e^- , NaOMe/MeOH ; (g) HClO_4 .

All the four stereoisomers of 3,7-dimethylnonadecane **69**, the sex pheromone of the alfalfa leaf mining beetle (*Agromyza frontella*), have been synthesised on the basis of derivatives of citronellol **6** and **19**.¹³ The key stage in this synthesis was the condensation of the chiral iodide **70** and sulfone **71**.

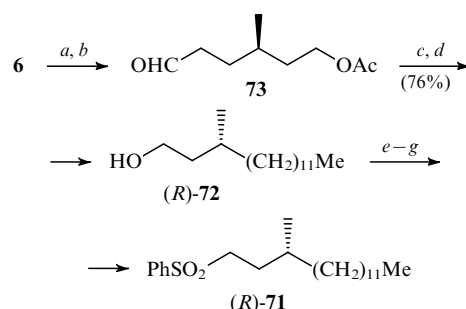


To obtain sulfone (*S*)-**71**, the alkylation product of the tosylate (*R*)-**19** was successively subjected to the Sharpless oxidation,⁸ ozonolysis, and reduction; the resulting alcohol (*S*)-**72** was converted into (*S*)-**71** by conventional procedures.



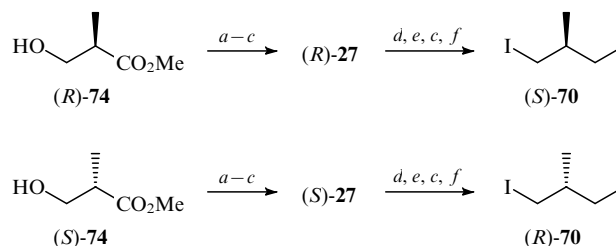
Reagents: (a) $\text{Me}(\text{CH}_2)_9\text{MgBr}/\text{Li}_2\text{CuCl}_4$; (b) $\text{Ph}_2\text{Se}_2/\text{H}_2\text{O}_2/\text{Bu}^t\text{OOH}$;
 (c) O_3/CHCl_3 ; (d) NaBH_4 ; (e) TsCl/Py ; (f) PhSNa/MeOH ;
 (g) MCPBA .

The (*R*)-enantiomer of the sulfone **71** was synthesised from the acetoxy aldehyde **73** derived from the compound **6** by ozonolysis and reduction. The Wittig alkenation of **73** and the subsequent hydrogenation of the intermediate alkene gave the alcohol (*R*)-**72**, which was converted into the sulfone (*R*)-**71** in a way analogous to that for the (*S*)-enantiomer.



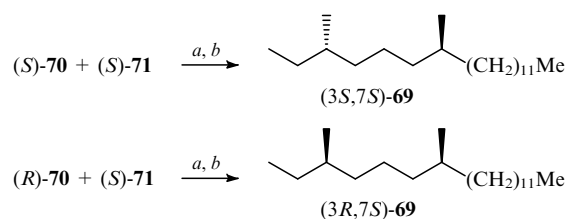
Reagents: (a) O_3/MeOH ; (b) Me_2S ; (c) $\text{Ph}_3\text{P}=\text{CH}(\text{CH}_2)_7\text{Me}$;
 (d) $\text{LiAlH}_4/\text{CoCl}_2$; (e) TsCl/Py ; (f) PhSNa/MeOH ;
 (g) MCPBA .

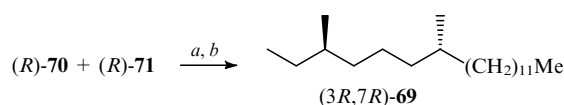
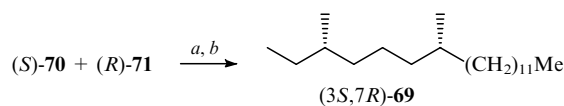
The synthesis of the chiral iodides **70** was carried out on the basis of the hydroxy esters **74** via the intermediate, selectively protected diols **27**.



Reagents: (a) DHP/TsOH ; (b) LiAlH_4 ; (c) TsCl/Py ;
 (d) $\text{MeMgBr}/\text{Li}_2\text{CuCl}_4$; (e) H_3O^+ ; (f) $\text{NaI}/\text{Me}_2\text{CO}$.

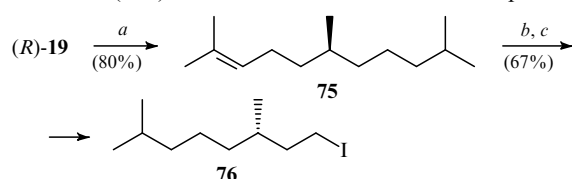
Reactions of the chiral sulfones **71** and iodides **70** in various combinations and subsequent desulfonation of the reaction products gave all four stereoisomers of the pheromone **69**.





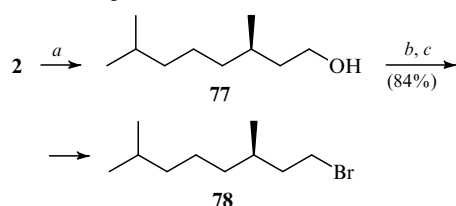
Reagents: (a) BuⁿLi; (b) Na–Hg.

The tosylate (*R*)-**19** has also found application in the synthesis of (2*R*,6*R*,10*R*)-6,10,14-trimethylpentadecan-2-ol **83**, the sex pheromone of the rice moth (*Corcyra cephalonica*) and its analogues having the (2*S*,6*R*,10*R*)-, (2*S*,6*S*,10*S*)-, or (2*R*,6*R*,10*S*)-configuration.¹⁴ The building block **76** obtained from **19** via the alkene **75**, which was subjected to periodate scission in the presence of catalytic amounts of RuCl₃, was used for the formation of the (10*S*)-chiral centre of the two latter compounds.



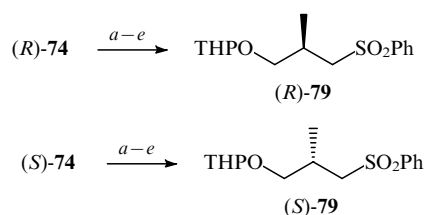
Reagents: (a) BuⁱMgBr/Li₂CuCl₄; (b) NaIO₄/RuCl₃; (c) I₂/Pd(OAc)₄/hν/CCl₄.

The formation of the (10*R*)-centre of the stereoisomers (2*R*,6*R*,10*R*)- and (2*S*,6*R*,10*R*)-**83** was carried out with the use of the bromide **78** obtained in high yield from dihydrocitronellol **77**, the reduction product of citronellic acid **2**.



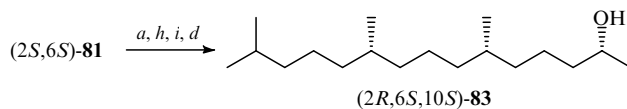
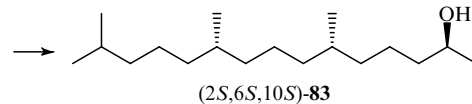
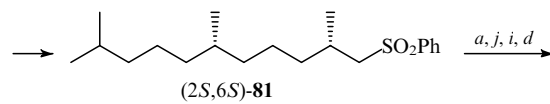
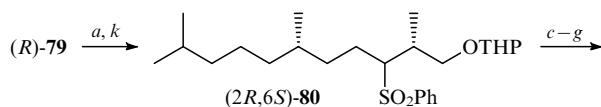
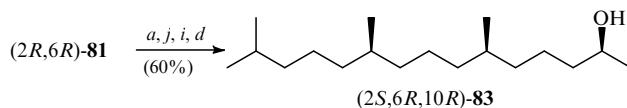
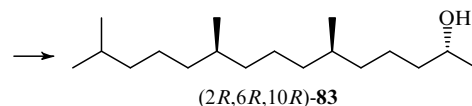
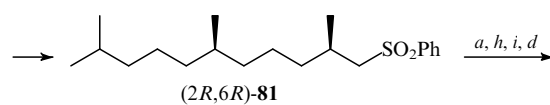
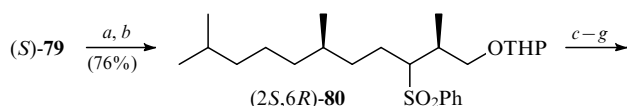
Reagents: (a) LiAlH₄/CoCl₂; (b) TsCl/Py; (c) NaBr/DMF.

The (*R*)- and (*S*)-sulfonyl chlorides **79** derived from (*R*)- and (*S*)-hydroxy acids **74** were used in the formation of (6*R*)- and (6*S*)-chiral centres of the corresponding stereoisomers **83**.



Reagents: (a) DHP/TsOH; (b) LiAlH₄; (c) TsCl/Py; (d) NaSPh; (e) MCPBA.

Different versions of alkylation of the chiral sulfonyl chlorides **79** with the iodide **76** or the bromide **78** with subsequent desulfonation of the corresponding condensation products **80**, their conversion into the sulfonyl chlorides **81** and analogous sequences of reactions of the stereoisomers **81** and enantiomeric iodohydrins **82** resulted in the four stereoisomers of the target compounds **83**.

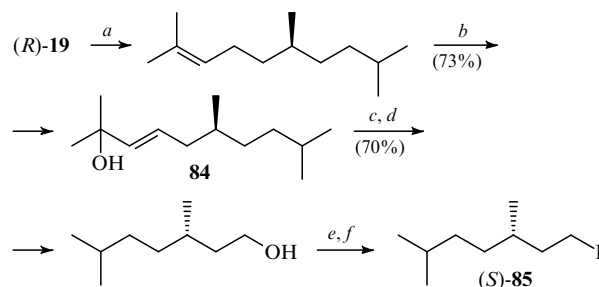


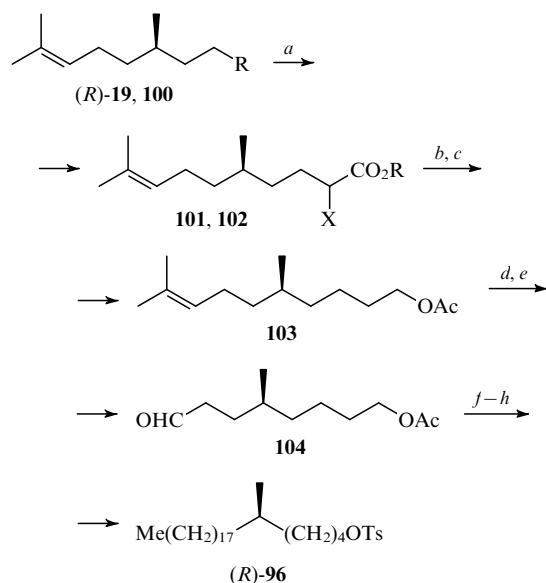
Reagents: (a) BuⁿLi; (b) **78**; (c) Na–Hg; (d) H₃O⁺; (e) TsCl/Py;

(f) NaSPh; (g) MCPBA; (h) (R)-**82**; (i) Li/EtNH₂;

(j) (S)-**82**; (k) **76**.

The obvious structural identity of the portion of 6,10,13-trimethyltetradecan-1-ol **87**, the aggregation pheromone of the predacious beetle (*Stiretrus anchorage*), with that of the above-described pheromone **83** has encouraged their application in the synthesis of its four optical isomers.¹⁵ The chiral building blocks **85** required for this purpose were prepared from citronellyl acetate (*S*)-**6** (following its ozonolysis) and the disubstituted alkene **84** synthesised from (*R*)-**19** by a two-step procedure.





R = OTs [(R)-19], I (100);

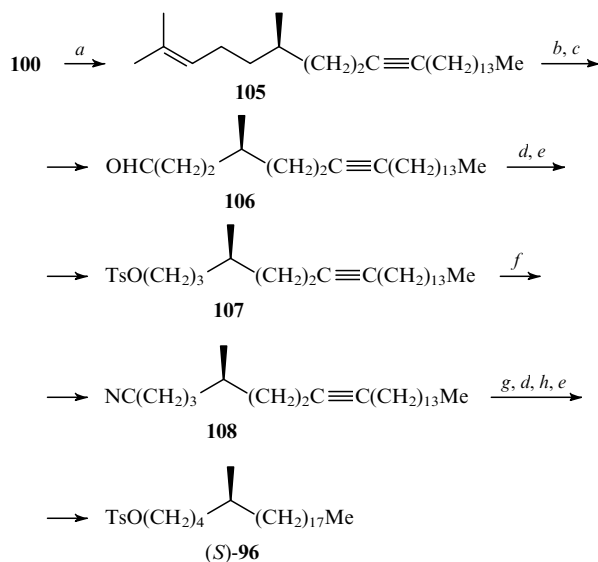
X = CO₂Et, R = Et (101); X = R = H (102).

Reagents: (a) CH₂(CO₂Et)₂/BuⁿLi; (b) LiAlH₄; (c) Ac₂O/Py;

(d) MCPBA; (e) HIO₄; (f) [Me(CH₂)₁₄PPh₃]Br/BuⁿLi;

(g) H₂/Pd; (h) TsCl/Py.

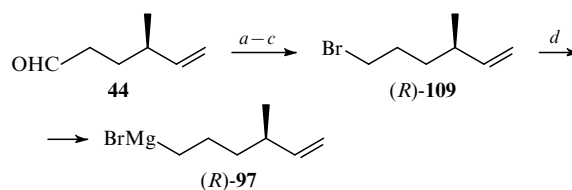
The tosylate (S)-96 was obtained from the product of alkylation of the iodide 100 with hexadec-1-ynyllithium. The enyne 105 was oxidised to the aldehyde 106 by cleavage of the double bond. The latter was further converted into the tosylate 107; its homologisation *via* the nitrile 108 completed the synthesis of the tosylate (S)-96.



Reagents: (a) HC≡C(CH₂)₁₃Me/BuⁿLi; (b) MCPBA; (c) HIO₄;

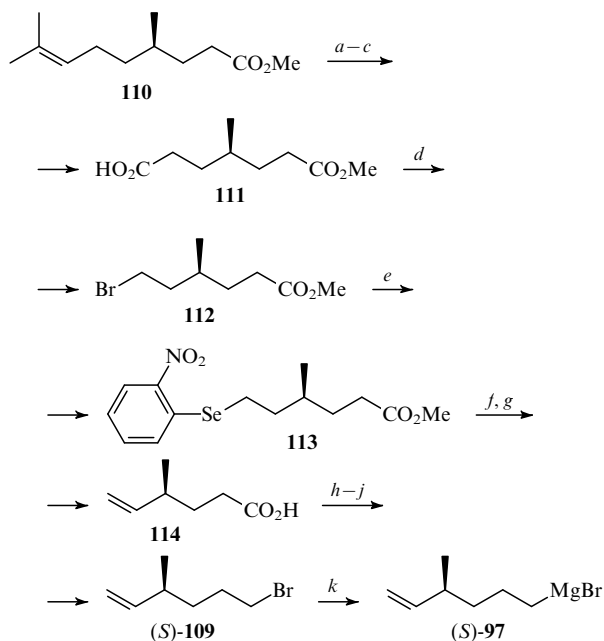
(d) LiAlH₄; (e) TsCl/Py; (f) NaCN; (g) NaOH; (h) H₂/Pd.

The bromide (R)-109 required for the synthesis of the Grignard reagent 97 was obtained from the aldehyde 44 by routine reactions.



Reagents: (a) LiAlH₄; (b) TsCl/Py; (c) LiBr; (d) Mg.

The bromide (S)-109 was prepared from methyl homocitronellate 110. Its ozonolysis and subsequent oxidation gave the acid 111. The methyl bromoalkanoate 112 obtained by the Hunsdiecker reaction was converted into the unsaturated acid 114 *via* the selenide 113. The bromide (S)-109 was synthesised from the acid 114 by standard procedures.

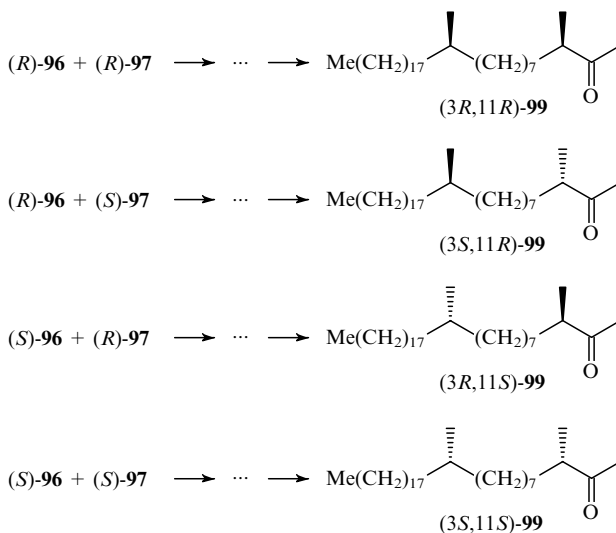


Reagents: (a) O₃/MeOH; (b) Me₂S; (c) CrO₃; (d) Ag₂O-Br₂;

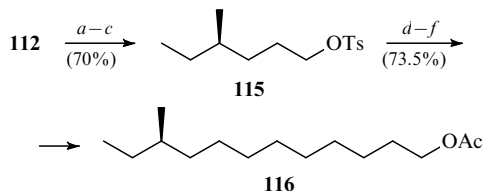
(e) 2-NO₂C₆H₄SeCN/NaBH₄; (f) NaOH; (g) H₂O₂;

(h) LiAlH₄; (i) TsCl/Py; (j) LiBr; (k) Mg.

Reactions of tosylates 96 with the Grignard reagents 97 followed by Markovnikov hydration of the corresponding alkenes and the oxidation of the resulting alcohols gave all the four stereoisomers of the pheromone 99.¹⁹

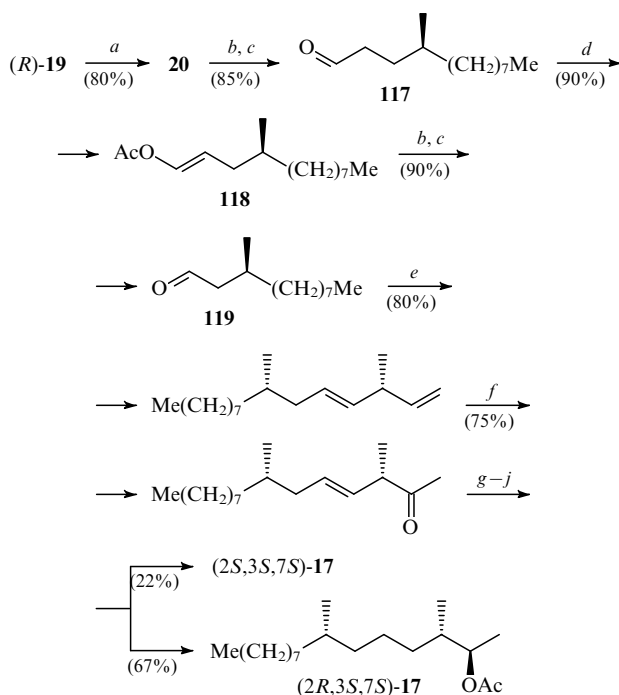


The methyl bromoalkanoate **112**, one of intermediate products in the scheme presented above, has also been employed in the synthesis of (10*R*)-methyl dodecyl acetate **116**, the minor component of the sex pheromone of the tea leaf rolling moth (*Adoxophyes fasciata*). The formation of the hydrocarbon chain of **116** was carried out by cross-coupling of the tosylate **115** obtained from the bromide **112** and the Grignard reagent **117**.²⁰



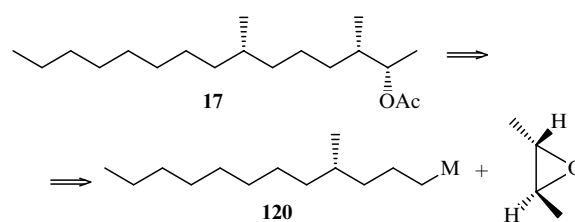
Reagents: (a) NaI; (b) LiAlH₄; (c) TsCl/Py; (d) BrMg(CH₂)₆OTHP/(**117**)/Li₂CuCl₄; (e) MeOH/TsOH; (f) Ac₂O/Py.

A formally two-step synthesis of *erythro*-(2*S*,3*S*,7*S*)- and *threo*-(2*R*,3*S*,7*S*)-diprionyl acetates **17** from the tosylate (*R*)-**19** has been carried out.²¹ The aim of the first step was the formation of the structure of the chiral aldehyde **119**; this was accomplished by ozonolysis of the alkene **20** to the aldehyde **117** followed by ozonolysis of the derived enol acetate **118**. The reactions used at the second step of the synthesis of the target acetates (2*S*,3*S*,7*S*)-**17** and (2*R*,3*S*,7*S*)-**17** did not differ from those depicted in Scheme 1 for the enantiomers having the (*R*)-configuration of the C(7) atom.^{4, 5}

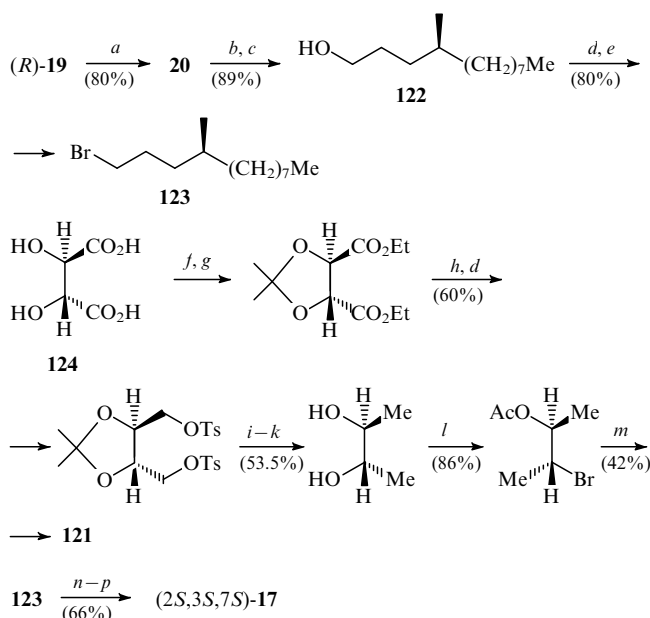


Reagents: (a) Me(CH₂)₅MgCl/CuI; (b) O₃/CH₂Cl₂-MeOH; (c) Me₂S; (d) Ac₂O/AcOK/Et₃N; (e) **12**/BuⁿLi; (f) O₂/PdCl₂-CuCl; (g) NaBH₄; (h) H₂/Pt; (i) HPLC; (j) Ac₂O/Et₃N/DMAP.

The retrosynthetic analysis of (2*S*,3*S*,7*S*)-diprionyl acetate **17** suggests that this compound can be obtained by the reaction of the organometallic nucleophile **120** with (*S*,*S*)-2,3-epoxybutane **121**.

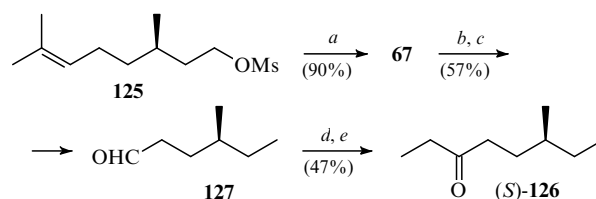


Mori *et al.*^{22, 23} have performed the synthesis of the bromide **123**, the chiral building block corresponding to the synthon **120**, by the following scheme. The coupling of the tosylate (*R*)-**19** with lithium dihexyl cuprate and subsequent ozonolysis of the alkene **20** gave the alcohol **122**, which was converted into the bromide by conventional methods. The complementary epoxide **121** was synthesised from the natural L-(+)-tartaric acid **124** in nine steps. The reaction of lithium dialkyl cuprate derived from the bromide **123** with the epoxide **121**, which occurred with high stereoselectivity with respect to all the three chiral centres, gave the target product, diprionyl acetate (2*S*,3*S*,7*S*)-**17**.



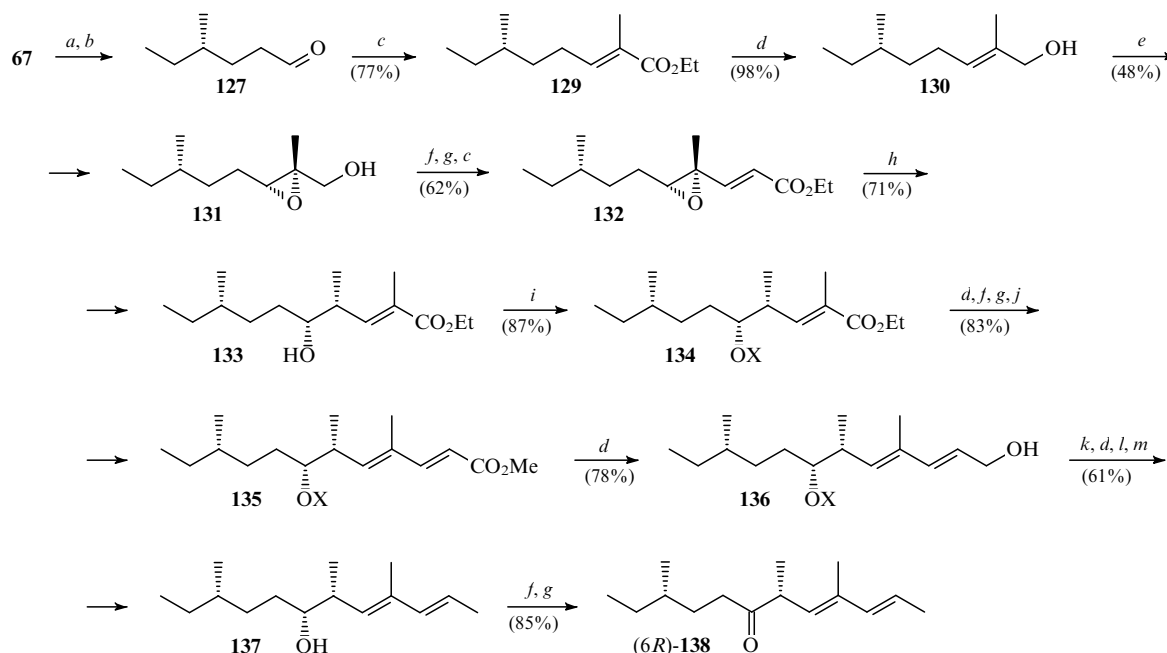
Reagents: (a) [Me(CH₂)₅]₂CuLi; (b) O₃/CHCl₃; (c) NaBH₄; (d) TsCl/Py; (e) LiBr; (f) EtOH/H⁺; (g) Me₂CO/H⁺; (h) LiAlH₄; (i) NaI; (j) H₂/Pd/C; (k) HCl; (l) HBr/AcOH; (m) KOH; (n) Li/CuI; (o) **121**; (p) AcCl/Py.

Tetrahydromyrcene **67** obtained by reduction of citronellyl mesylate **125** was used in the synthesis of (6*S*)-methyloctan-3-one, (*S*)-**126**, the component of the alarm pheromone of ants of the *Crematogaster* genus.²⁴



Reagents: (a) LiAlH₄; (b) MCPBA; (c) HIO₄; (d) EtMgBr; (e) K₂Cr₂O₇.

Scheme 6



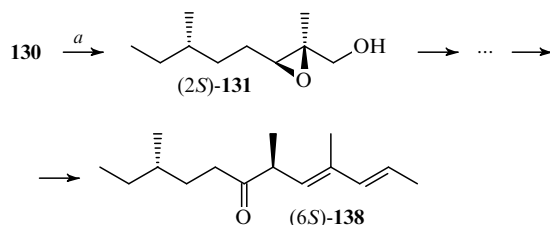
X = SiMe₂Bu^t.

Reagents: (a) O₃/NaHCO₃; (b) Me₂S; (c) Ph₃P=C(Me)CO₂Et (**128**); (d) LiAlH₄; (e) D-(−)-diethyl tartrate [D-(−)-DET]/Ti(OPrⁱ)₄/Bu^tOOH; (f) (COCl)₂–DMSO; (g) Et₃N; (h) [Pd(dba)₃·CHCl₃]/PPh₃ (dba is dibenzoylacetone); (i) Bu^tMe₃SiCl/imidazole; (j) (MeO)₂P(O)CH₂COOMe/BuⁿLi; (k) SO₃/Py; (l) Bu₄NF; (m) HPLC.

(2*E*,4*E*,6*R*,10*S*)-4,6,10-Trimethyl-2,4-dodecadien-7-one, (6*R*)-**138**, and its (6*S*,10*S*)-isomer, (6*S*)-**138**, the major components of the sex pheromone of the cluster pine scale (*Matsucoccus feytaudi*), have been synthesised using the same building block **67**.²⁵ This synthesis is based on enantioselective epoxidation of the trisubstituted allylic alcohol **130** obtained by a series of transformations from the alkene **67**. The reaction sequence includes ozonolysis and reduction, the Wittig condensation of the resulting aldehyde **127** with the phosphorane **128**, and subsequent reduction of the ester **129** with LiAlH₄. The conversion of the hydroxy group of compound (2*R*)-**131** into the aldehyde group and Wittig alkenation gave the compound **132**; the opening of its epoxide ring resulted in the inversion of the C(4) chiral centre. All subsequent conversions of the compound **133** into the compound (6*R*)-**138** occurred with the retention of the configurations of the carbon atoms. The Horner reaction was used to complete the carbon chain of the compound **133** (Scheme 6).

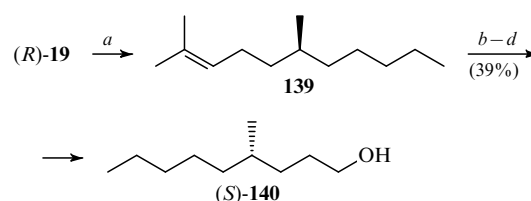
The use of L-(+)-diethyl tartrate in an analogous scheme at the epoxidation stage gave the (6*S*,10*S*) isomer of **138** via the compound (2*S*)-**131** (Scheme 7).

Scheme 7



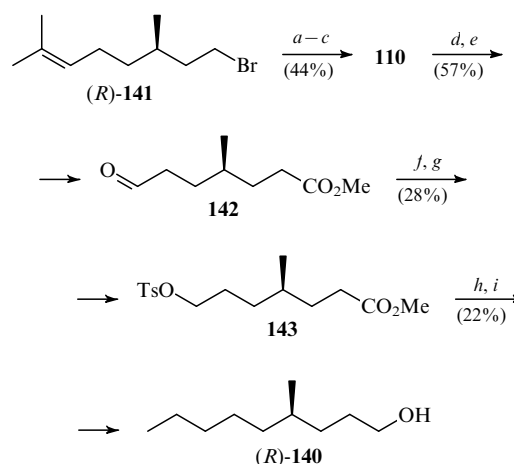
Reagents: (a) L-(+)-DET/Ti(OPrⁱ)₄/Bu^tOOH.

Both stereoisomers of 4-methylnonan-1-ol **140** the (*R*)-enantiomer of which is the sex pheromone of the mealworm (*Tenebrio molitor* L.), have been synthesised from citronellyl tosylate (*R*)-**19** and citronellyl bromide **141**.²⁶ The isomer (*S*)-**140** was obtained through oxidative scission of the double bond in the compound **139**, the condensation product of the tosylate (*R*)-**19** with PrⁿMgBr.



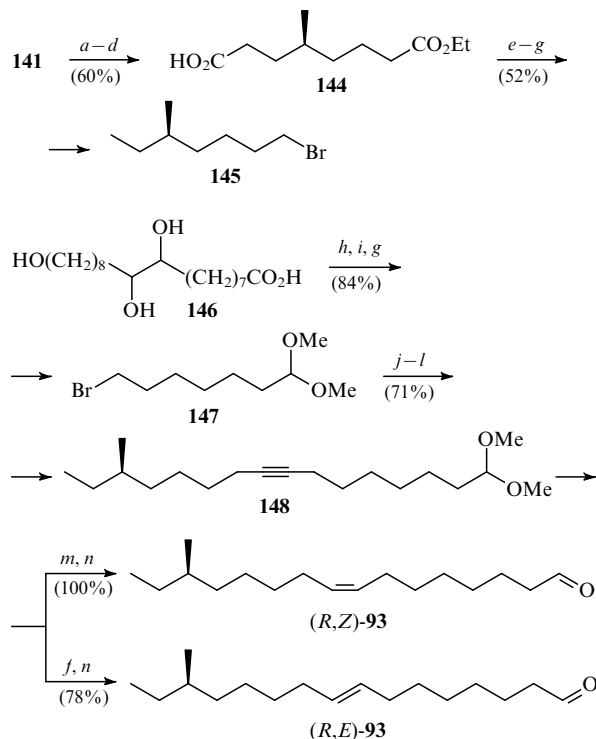
Reagents: (a) PrⁿMgBr/Li₂CuCl₄; (b) MCPBA; (c) HIO₄; (d) LiAlH₄.

The synthesis of the enantiomer (*R*)-**140** was carried out according to the scheme that involved the conversion of (*R*)-**141** into methyl homocitronellate **110** and oxidative scission of the double bond to give the aldehyde **142**, which was made to react with Et₂CuLi after conversion into the tosylate **143**. The reduction of the carboxyl group yields the target product.



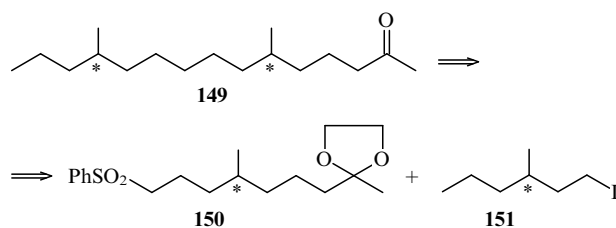
Reagents: (a) Mg; (b) CO₂; (c) MeOH/H₂SO₄; (d) MCPBA; (e) HIO₄; (f) NaBH₄; (g) TsCl/Py; (h) Et₂CuLi; (i) LiAlH₄.

The bromide **141** has proved to be a convenient starting material in the synthesis of the *Z*- and *E*-isomers of (*R*)-trogodermal **93**.²⁷ The conversion of **141** into the chiral synthon **145** involved the 'malonate' synthesis and ozonolysis with subsequent oxidation leading to the monoester of the dicarboxylic acid **144**. The achiral block **146** was obtained by oxidative scission of aleuritic acid **146**. Successive alkylation of sodium acetylide with the bromide **147** and of the reaction product, with the chiral bromide **145** yielded the alkyne **148**, the precursor of the target pheromones, which were obtained by stereoselective hydrogenation.



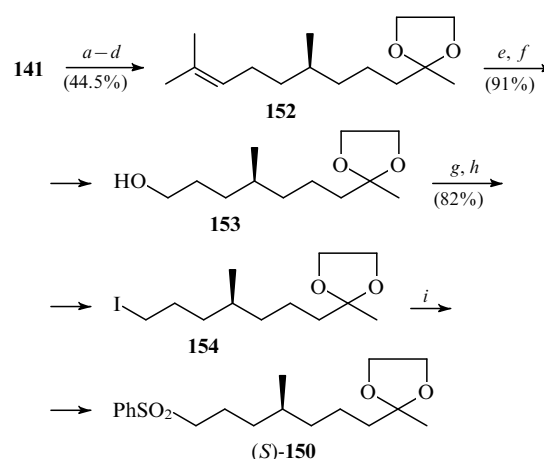
Reagents: (a) $\text{NaCH}(\text{CO}_2\text{Et})_2$; (b) $\text{LiCl}/\text{H}_2\text{O}$; (c) O_3/MeOH ; (d) H_2CrO_4 ; (e) $\text{AgNO}_3/\text{K}_2\text{S}_2\text{O}_8$; (f) LiAlH_4 ; (g) $\text{Br}_2 \cdot \text{PPh}_3$; (h) NaIO_4 ; (i) MeOH/HCl ; (j) $\text{HC} \equiv \text{CNa}$; (k) Bu^nLi ; (l) **145**; (m) $\text{H}_2/\text{Ni P-2}$; (n) pyridinium *p*-toluenesulfonate (PPTs)/ H_2O .

The same bromide (*R*)-**141** has been used in the synthesis of all the stereoisomers of 6,12-dimethylpentadecan-2-one **149**, the sex pheromone of the cucumber flea beetle (*Diabrotica balteata* LeConte). The key stage in this synthesis was the alkylation of the sulfone **150** with the iodide **151**.²⁸



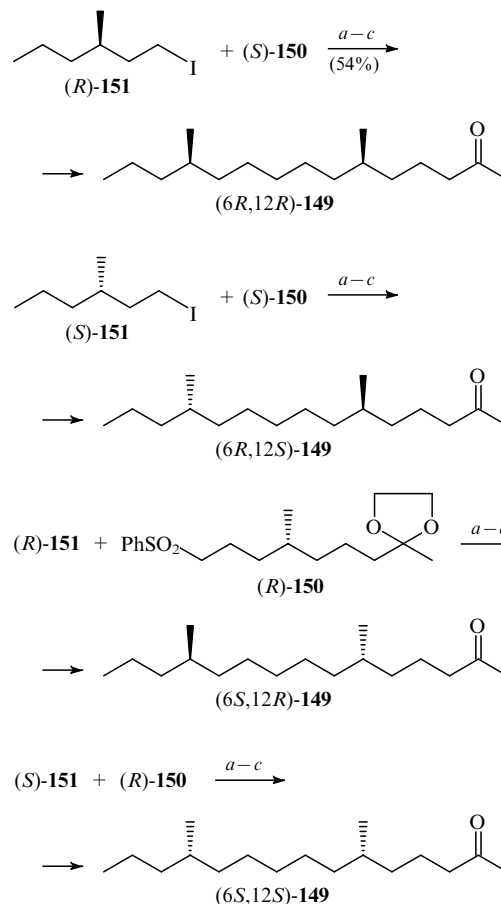
The (*R*)- and (*S*)-enantiomers of the iodide **151** were prepared as described.²⁹

In the synthesis of the sulfone (*S*)-**150**, the bromide (*R*)-**141** was first converted into the ketal **152**; its ozonolysis and reduction gave the alcohol **153**. The latter was converted into (*S*)-**150** via the iodide **154**. The (*R*)-sulfone **150** was synthesised from citronellyl bromide (*S*)-**141** by an analogous scheme.



Reagents: (a) $\text{CH}_3\text{CO}_2\text{Et}/\text{NaH}$; (b) KOH ; (c) HCl ; (d) O_3/TsOH ; (e) O_3 ; (f) NaBH_4 ; (g) TsCl/Py ; (h) $\text{NaI}/\text{NaHCO}_3$; (i) NaSO_2Ph .

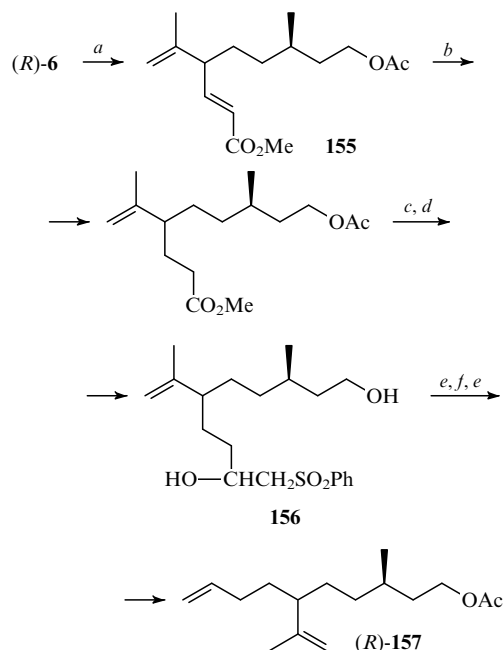
Different variants of the coupling of the sulfones (*R*)- and (*S*)-**150** with the iodides (*R*)- and (*S*)-**151** gave, after desulfonation of the condensation products, all the four optical isomers of **149**.



Reagents: (a) Bu^nLi ; (b) $\text{Na}-\text{Hg}$; (c) $\text{HCl}-\text{H}_2\text{O}$.

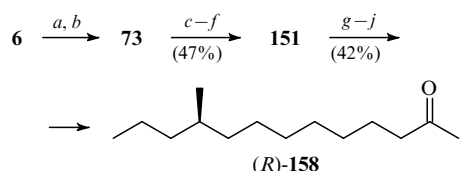
The synthesis of 6-isopropenyl-(3*R*)-methyldec-9-enyl acetate, (*R*)-**157**, the sex pheromone of the California red scale (*Aonidiella aurantii*), from (*R*)-citronellyl acetate **6** has been carried out.³⁰ The key stage in this synthesis was the AlCl_3 -catalysed reaction of methyl propionate with the acetate **6**, which occurred with double bond migration to the terminal position to give the diester **155** (a 1:1 diastereoisomeric mixture). The

selective reduction of the conjugated double bond in **155** and the subsequent building of the butenyl fragment *via* the intermediate hydroxysulfone **156** yielded the target product, (*R*)-**157**. An analogous synthesis from (*S*)-citronellyl acetate **6** gives (*S*)-**157**.



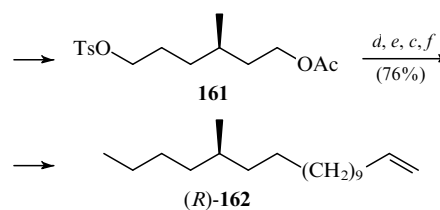
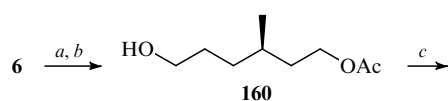
Reagents: (a) $\text{HC}\equiv\text{CCO}_2\text{Me}/\text{AlCl}_3$; (b) $\text{Fe}(\text{CO})_5/\text{NaOH}$; (c) $\text{PhSO}_2\text{CH}_2\text{Li}$; (d) NaBH_4 ; (e) $\text{Ac}_2\text{O}/\text{Py}$; (f) $\text{Na}-\text{Hg}$.

Ozonolysis of the acetate **6** and reduction give the acetoxy aldehyde **73**, which was used in the synthesis of (10*R*)-methyltridecan-2-one **158**, the pheromone of the Western spotted cucumber beetle (*Diabrotica undecimpunctata howardi*). After Wolff–Kishner reduction, the acetoxy aldehyde **73** was converted into the iodide **151**; its coupling with the complementary synthon **159** and conventional procedures gave the target ketone (*R*)-**158**.^{29, 31}



Reagents: (a) O_3/MeOH ; (b) Me_2S ; (c) $\text{NH}_2\text{NH}_2\cdot\text{H}_2\text{O}$; (d) KOH ; (e) TsCl/Py ; (f) NaI ; (g) $\text{LiC}\equiv\text{C}-\text{CH}_2\text{CH}_2\text{CH}_2\text{OTHP}$ (**159**); (h) H_3O^+ ; (i) $\text{H}_2/\text{Pd}/\text{C}$; (j) H_2CrO_4 .

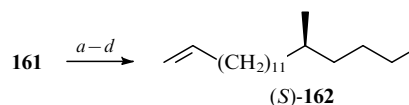
Yet another product of ozonolysis and reduction of the compound (*R*)-**6**, the hydroxyacetate **160**, was converted into the tosylate **161** and used in the synthesis of (14*R*)-methyloctadec-1-ene **162**, the antipode of the sex pheromone of the peach leaf mining beetle (*Lyonetia clerkella*).³² Successive alkylation with lithium dimethyl and di(undec-10-enyl) cuprates completed the synthesis of the enantiomer (*R*)-**162**.



Reagents: (a) O_3/MeOH ; (b) NaBH_4 ; (c) TsCl/Py ; (d) Me_2CuLi ; (e) NaOH/MeOH ; (f) $[\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_9]_2\text{CuLi}$.

In the synthesis of the pheromone (*S*)-**162**, the tosylate **161** was alkylated in the reverse order: at first, the alkene fragment of the molecule was built (Scheme 8) and then the reaction with lithium diethyl cuprate was carried out after the conversion of the acetyl group into the tosyl group.³²

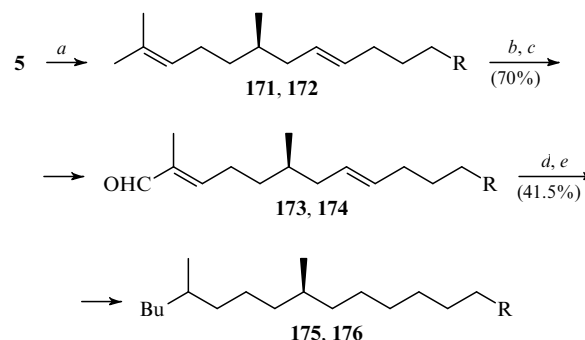
Scheme 8



Reagents: (a) $[\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_8]_2\text{CuLi}$; (b) NaOH/MeOH ; (c) TsCl/Py ; (d) Et_2CuLi .

The allylic alcohol **163** formed by the Sharpless oxidation⁸ of the acetate **6** was used in the synthesis of (2*R*,8*R*)- and (2*S*,8*R*)-stereoisomers of 8-methyldec-2-yl propionate **170**, the pheromone of the Western flea beetle (*Diabrotica virgifera virgifera*), for the introduction of the (8*R*)-chiral centre.³³ To this end, compound **163** was converted into the bromide **164**. The hydroxy ester (*R*)-**166** prepared by hydrolysis of the (*R*)-poly-β-hydroxybutyrate **165** was used as the key compound in the synthesis of the second chiral fragment. Its antipode, (*S*)-**166**, was obtained by enzymic reduction of the oxo ester **167**. Successive alkylation of the dithiane **168**, first with the bromide **164** and then with the (*R*)- or (*S*)-iodides **82** and subsequent desulfonation of the compounds **169a** and **169b** gave the esters (2*R*,8*R*)- and (2*S*,8*R*)-**170**, respectively (Scheme 9).

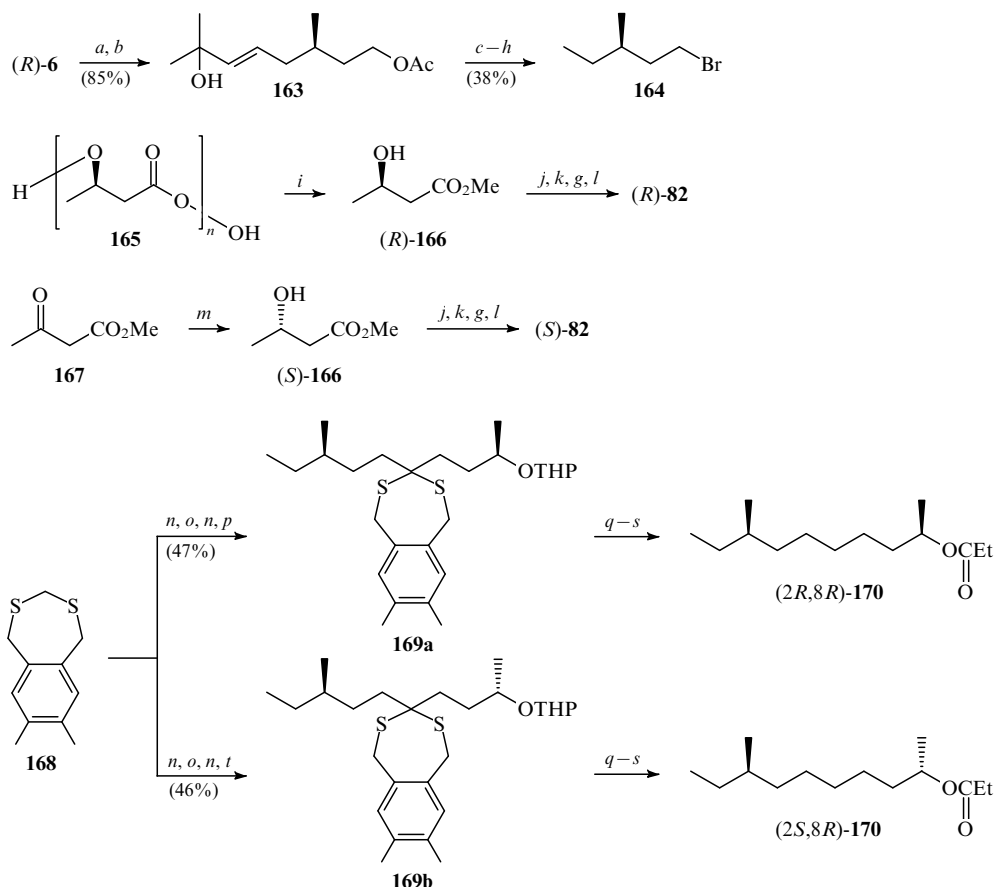
(5*S*/*R*,9*S*)-Dimethylheptadecane **175** and (5*S*/*R*,9*S*)-dimethylpentadecane **176**, the sex pheromones of *Leucoptera scitella* and *Perileucoptera coffeella*, respectively, have been synthesised from the citronellal **5**. The synthetic schemes involved the Wittig alkenation of the aldehyde **5**, selective allylic oxidation of the reaction products **171** and **172**, and repeated alkenation of the resulting aldehydes **173** and **174**.³⁴



$\text{R} = \text{H}$ (**172**, **174**, **176**, **178**), Et (**171**, **173**, **175**, **177**).

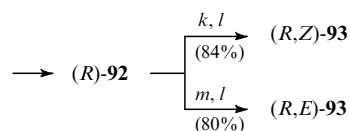
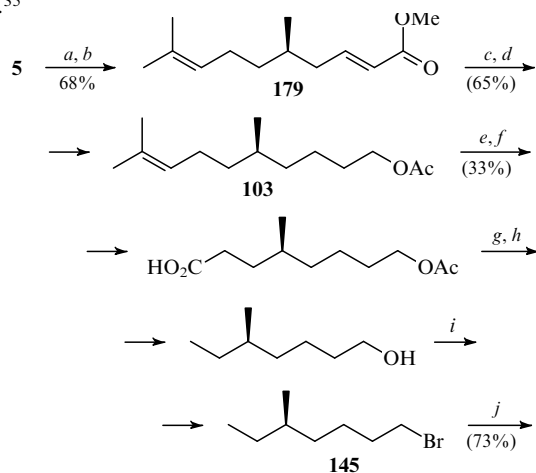
Reagents: (a) $[\text{R}(\text{CH}_2)_4\text{PPh}_3]\text{Br}$ (**177**, **178**)/ NaOMe ; (b) SeO_2 ; (c) PCC ; (d) $[\text{Pr}^n\text{PPh}_3]\text{Br}/\text{NaOMe}$; (e) $\text{H}_2/\text{Pd}/\text{C}$.

Scheme 9



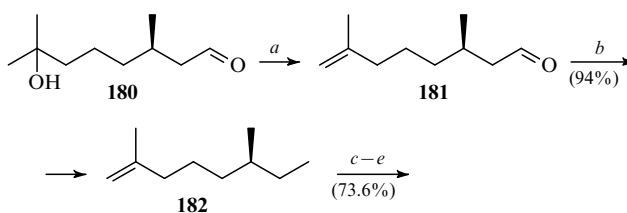
Reagents: (a) $\text{Ph}_2\text{Se}_2/\text{H}_2\text{O}_2$; (b) Bu^tOOH ; (c) O_3/MeOH ; (d) Me_2S ; (e) $\text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{O}$; (f) $\text{KOH}/\text{H}_2\text{O}$; (g) TsCl/Py ; (h) LiBr ; (i) $h\nu/\text{H}_3\text{O}^+$; (j) DHP/TsOH ; (k) LiAlH_4 ; (l) NaI ; (m) baker's yeast; (n) Bu^nLi ; (o) **164**; (p) **(R)-82**; (q) $\text{Raney Ni (Ni-Ra)}/\text{EtOH}$; (r) H_3O^+ ; (s) EtCOCl/Py ; (t) **(S)-82**.

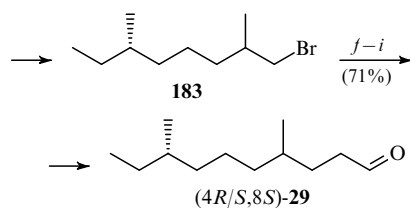
The citronellal **(R)-5** has also been employed in the synthesis of *Z*- and *E*-isomers of trogodermal **(R)-93**. The aldehyde **5** was condensed with malonic acid according to Doebner and then the dienic ester **179** was converted into the *Z*- or *E*-alkenes **93** by a reaction sequence that included the reduction of the double bond conjugated with the ester group, ozonolysis, and oxidation of the acetate **103** as well as stereoselective hydrogenation of the alkyne **92**.³⁵



Reagents: (a) $\text{CH}_2(\text{CO}_2\text{H})_2$; (b) MeOH/TsOH ; (c) $\text{Li}/\text{NH}_3/\text{EtOH}$; (d) $\text{Ac}_2\text{O}/\text{Py}$; (e) O_3 ; (f) CrO_3 ; (g) $\text{K}_2\text{S}_2\text{O}_8/\text{AgNO}_3$; (h) KOH ; (i) $\text{Br}_2 \cdot \text{PPh}_3$; (j) $\text{LiC} \equiv \text{C}(\text{CH}_2)_7\text{OTHP}$; (k) $\text{H}_2/\text{Ni-Ra}$; (l) PCC ; (m) $\text{Na}/\text{NH}_3/\text{EtOH}$.

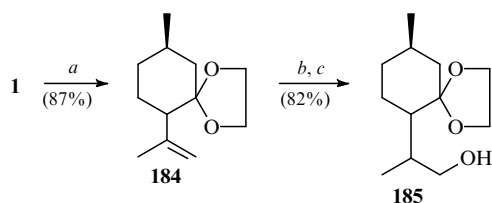
The citronellal derivative **(R)-180** served as the starting material in the synthesis of 4,8-dimethyldecanal **29**, configurationally homogeneous with respect to the C(8) atom.³⁶ The dehydration of the hydroxy aldehyde **180** gave the rodinal **181**, which was converted by the Wolff–Kishner reaction into the alkene **182**. Homologisation of the bromide **183** derived from the compound **182** by a two-step procedure has opened the way to the target product, **(4R/S,8S)-29**.





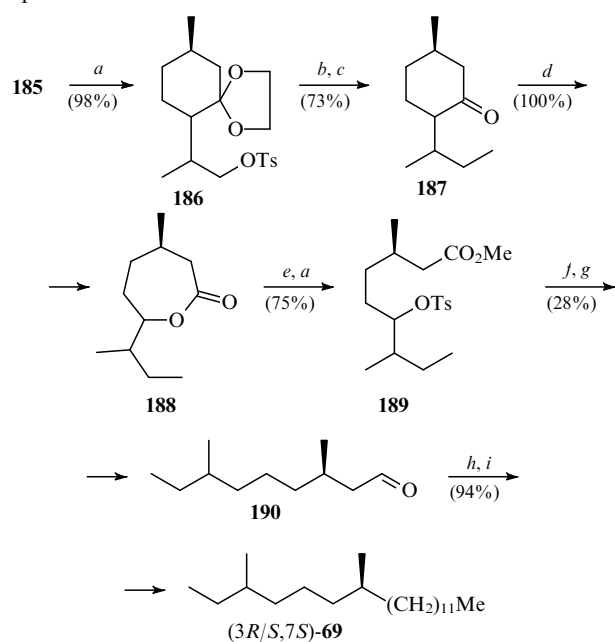
Reagents: (a) Al_2O_3 , 350 °C; (b) $\text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{O}/\text{KOH}$; (c) B_2H_6 ; (d) $\text{H}_2\text{O}_2/\text{NaOH}$; (e) $\text{Br}_2 \cdot \text{PPh}_3$; (f) $\text{CH}_2(\text{CO}_2\text{Et})_2/\text{NaH}$; (g) AcOK ; (h) LiAlH_4 ; (i) PCC .

The transformation of pulegone **1** involving the Baeyer–Williger reaction was used in the synthesis of two stereoisomeric 3,7-dimethylnonadecanes, (3*R*,7*R*/*S*)- and (3*R*/*S*,7*S*)-**69**.³⁷ The introduction of the protective ketal group under conditions of acid catalysis was accompanied by a migration of the double bond in the compound **1** to the terminal position. Hydroboration of the resulting α -alkene **184** and subsequent oxidation gave the alcohol **185**, the starting compound for both syntheses.



Reagents: (a) $(\text{CH}_2\text{OH})_2/\text{TsOH}$; (b) B_2H_6 or 9-BBN; (c) $\text{H}_2\text{O}_2/\text{NaOH}$.

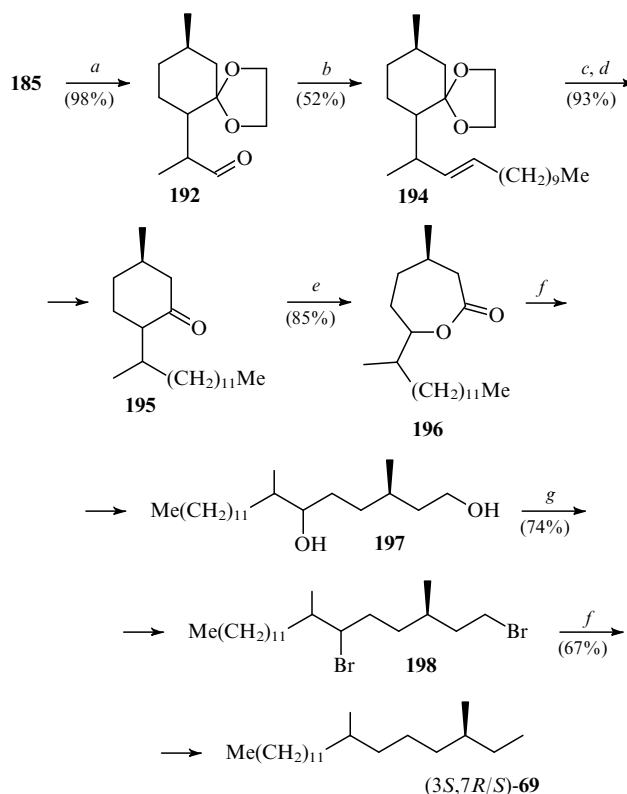
To obtain the stereoisomer (3*R*/*S*,7*S*)-**69**, the hydroxy acetal **185** was converted into the ketone **187** via the tosylate **186**. The lactone **188**, prepared from the ketone by a regioselective Baeyer–Williger reaction, was converted into (3*R*/*S*,7*S*)-**69** by a sequence of reactions that involved acid cleavage of **188**, simultaneous reduction of the ester and tosyloxy groups in the compound **189**, and the Wittig reaction between the aldehyde **190** and the phosphorane **191**.³⁷



Reagents: (a) TsCl/Py ; (b) Me_2CuLi ; (c) $\text{HCl}-\text{H}_2\text{O}$; (d) MCPBA ; (e) $\text{MeOH}/\text{H}_2\text{SO}_4$; (f) LiAlH_4 ; (g) PCC ; (h) $\text{Me}(\text{CH}_2)_8\text{CH}=\text{PPh}_3$ (**191**); (i) $\text{H}_2/\text{Pd}/\text{C}$.

In the synthesis of the isomer (3*S*,7*R*/*S*)-**69**, the aldehyde **192** obtained from the alcohol **185** was alkenated with the ylide **193**. The reaction product **194** was converted into the ketone **195**,

which was then oxidised by the Baeyer–Williger reaction. The resulting lactone **196** was converted into the diol **197** and further into the dibromide **198**; its hydride reduction gave (3*S*,7*R*/*S*)-**69**.³⁷



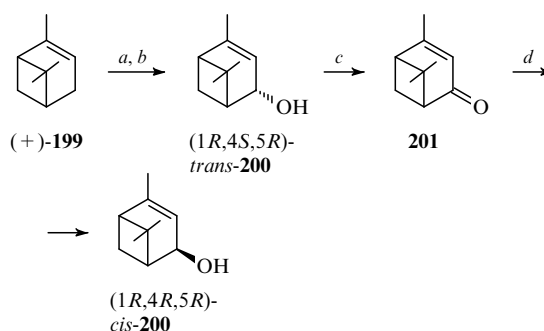
Reagents: (a) PCC ; (b) $\text{Me}(\text{CH}_2)_9\text{CH}=\text{PPh}_3$ (**193**); (c) $\text{H}_2/\text{Pt}/\text{O}_2$; (d) $\text{HCl}-\text{H}_2\text{O}$; (e) MCPBA ; (f) LiAlH_4 ; (g) $\text{Br}_2 \cdot \text{PPh}_3$.

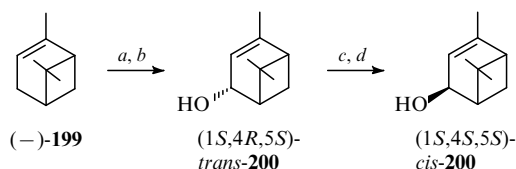
III. Syntheses on the basis of α - and β -pinenes

In the syntheses of pheromones, α - and β -pinenes have also been employed. The methods of their functionalisation can be divided into three groups: (1) reactions without scission of the rings; (2) reactions with the retention of the small (four-membered) ring, and (3) reactions with the opening of both rings.

1. Reactions without scission of the rings

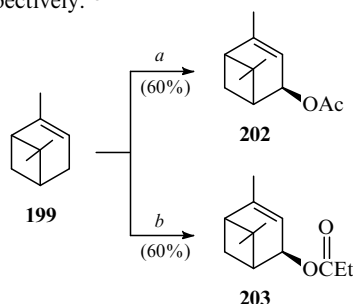
An example of the first type of conversions is the synthesis of *cis*- and *trans*-verbenols **200** constituting the aggregation pheromones of many species of bark beetles of *Ips* and *Dendroctonus* genera. Chiral *trans*-**200** were obtained by allylic oxidation of the corresponding enantiomers of α -pinene **199**,^{38,39} whereas *cis*-**200**, by the Jones oxidation of *trans*-verbenol **200** into verbenones **201** with subsequent reduction with NaBH_4 ^{40,41} or LiAlH_4 .⁴²





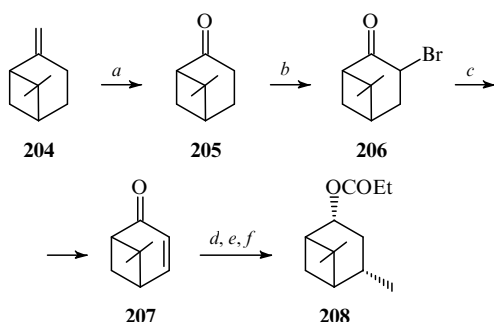
Reagents: (a) $\text{Pb}(\text{OAc})_4$; (b) OH^- ; (c) $\text{H}_2\text{Cr}_2\text{O}_7$; (d) NaBH_4 or LiAlH_4 .

The effective cockroach attractants, *cis*-verbenyl acetate **202** and *cis*-verbenyl propionate **203**, have been synthesised by oxidation of α -pinene **199** with lead tetraacetate or tetrapropionate, respectively.⁴³



Reagents: (a) $\text{Pb}(\text{OAc})_4$; (b) $\text{Pb}(\text{OCOEt})_4$.

Nopinone **205**, the product of ozonolysis of β -pinene **204**, has found wide application in the synthesis of insect pheromones.^{44–46} For example, the bicyclic propionate **208** possessing the activity of the sex pheromone of cockroaches, was prepared by transformation of the ketone **205** into apoverbenone **207** via the corresponding monobromide **206**.⁴⁴

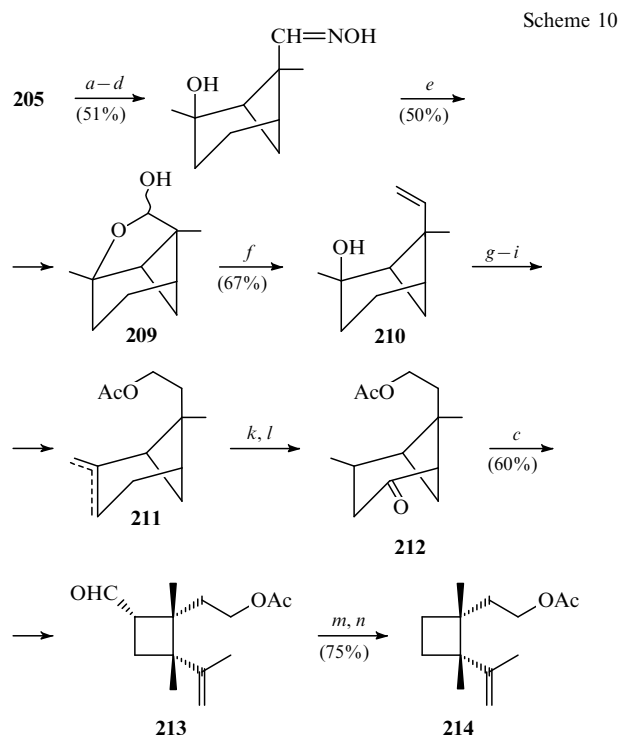


Reagents: (a) O_3/MeOH ; (b) Br_2 ; (c) 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU); (d) Me_2CuLi ; (e) $(\text{Pr}^i\text{O})_3\text{Al}/\text{Pr}^i\text{OH}$; (f) $(\text{EtCO})_2\text{O}$.

2. Reactions with the retention of the four-membered ring

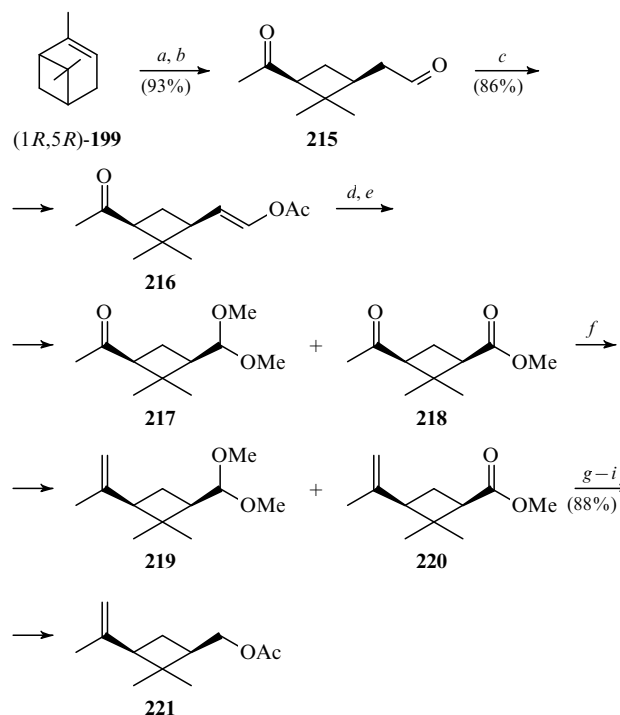
The ketone **205** has also served as the starting material in the synthesis of (+)-grandisol **214**, the aggregation-sex pheromone of the boll weevil (*Anthonomus grandis*).^{47, 48} The lactol **209** prepared from the ketone **205** by a five-step procedure was converted by the Wittig reaction into the alkene **210** and then, by a series of simple reactions, into a mixture of alkenes **211**; their allylic oxidation and subsequent hydrogenation gave the ketone **212**. The Norrish photocleavage of this compound followed by deformylation of the resulting aldehyde **213** with the Wilkinson complex and the removal of acetate protection eventually resulted in the target pheromone, (1*R*,2*S*)-**214** (Scheme 10).

The scission of α -pinene **199** with the retention of the small ring was employed in the synthesis of (+)-(1*R*,3*R*)-1-acetoxy-methyl-3-isopropenyl-2,2-dimethylcyclobutane **221**, the sex pheromone of the citrus mealybug (*Planococcus citri*).^{49, 50} This involved the ozonolysis of **199** to yield the oxo aldehyde **215** with the configuration of the chiral centres identical with that of the natural pheromone. The necessary shortening of the side chain was carried out via the enol acetate **216**; its ozonolysis gave a



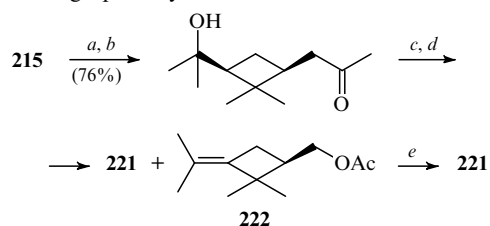
Reagents: (a) MeMgBr ; (b) NOCl ; (c) $h\nu$; (d) Δ ; (e) H_3O^+ ; (f) $\text{H}_2\text{C}=\text{PPh}_3$; (g) R_2BH ; (h) $\text{H}_2\text{O}_2/\text{NaOH}$; (i) $\text{Ac}_2\text{O}/\text{Py}$; (j) POCl_3/Py ; (k) $\text{CrO}_3 \cdot \text{Py}$; (l) $\text{H}_2/\text{Pd/C}$; (m) $(\text{PPh}_3)_3\text{RhCl}$; (n) LiAlH_4 .

mixture of the acetal **217** and the ester **218**. Treatment of this mixture with methylenephosphorane yielded a mixture of **219** and **220** further converted into the acetate **221** by a three-step procedure. Compound (–)-**221** was synthesised from α -(–)-pinene according to the same scheme.⁵¹



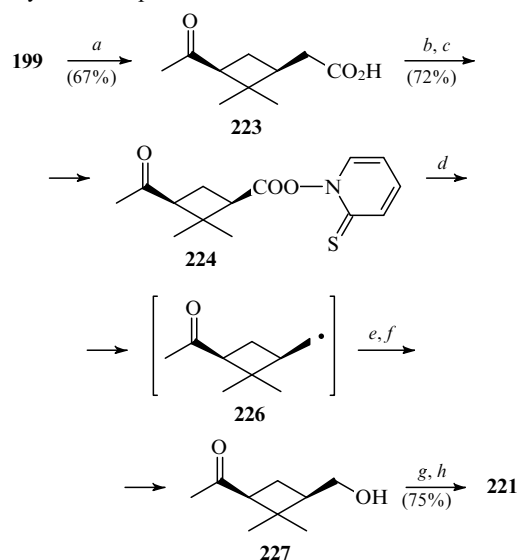
Reagents: (a) O_3/MeOH ; (b) $\text{H}_2/\text{Pd}/\text{CaCO}_3/\text{PbO}$; (c) $\text{Ac}_2\text{O}/\text{NEt}_3$; (d) O_3/SiO_2 ; (e) MeOH/TsOH ; (f) $\text{H}_2\text{C}=\text{PPh}_3$; (g) $\text{PPTs}/\text{H}_2\text{O}$; (h) Bu_2AlH ; (i) $\text{Ac}_2\text{O}/\text{Py}$.

The oxo aldehyde **215** is the key compound in yet another scheme of the synthesis of the compound **221** in which the final stage produced a mixture of acetates **221** and **222** separated chromatographically.⁵²



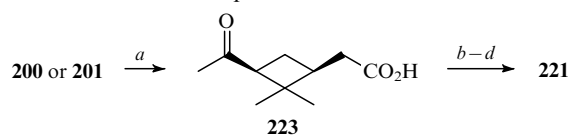
Reagents: (a) MeMgI; (b) CrO₃; (c) PhCO₃H; (d) POCl₃/Py; (e) SiO₂/AgNO₃.

The pheromone **221** has also been synthesised from the oxo acid **223**, another oxidation product of α -pinene **199**. Irradiation of the product of its reaction with *N*-hydroxy-2-thiopyridine with a tungsten-lamp light gave the intermediate radical **226**; its catalytic oxidation with oxygen and subsequent hydrolysis yielded the alcohol **227**. It was then converted into the target compound **221** by standard procedures.⁵³



Reagents: (a) KMnO₄/(NH₄)₂SO₄/H₂O; (b) SO₂Cl₂; (c) HO-N₂ (225); (d) hv/CH₂Cl₂; (e) O₂/Ph₂SbS(2-MeOC₆H₄); (f) H₂O; (g) Ac₂O/Py; (h) H₂C=PPh₃.

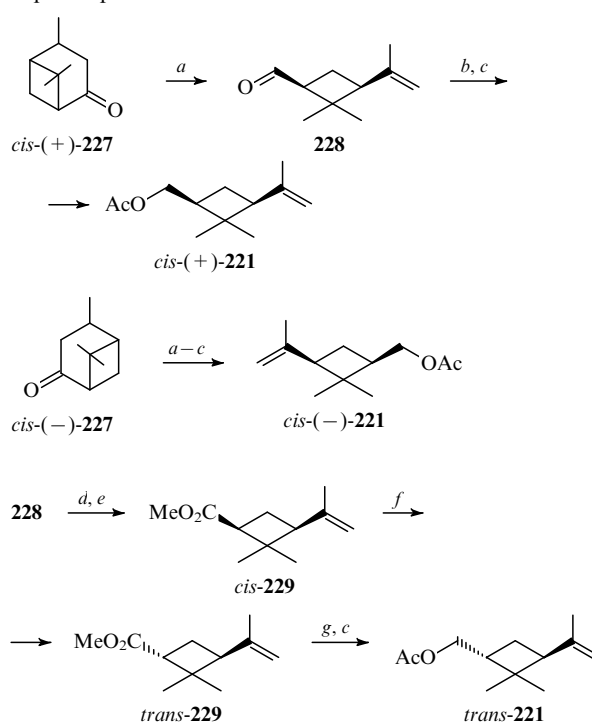
Yet another synthesis of **221** is based on the use of the oxo acid **223**, the product of the oxidative cleavage of (+)-verbenone **201** or *cis*- and *trans*-verbenols **200** with ruthenium chloride in combination with sodium periodate.⁵⁴



Reagents: (a) RuCl₃·3H₂O/NaIO₄; (b) H₂C=PPh₃; (c) LiAlH₄; (d) Ac₂O/Et₃N.

The cyclic aldehyde **228**, the photolysis product of *cis*-(+)-verbanone **227**, has also found application in the synthesis of *cis*-(+)-**221**. The *cis*-(-)-isomer **221** was obtained from *cis*-(-)-verbanone **227** in an analogous way. The *trans*-isomer **221** was

synthesised by conversion of **228** into the *cis*-ester **229** with its subsequent epimerisation into the *trans*-isomer **229**.⁵⁵

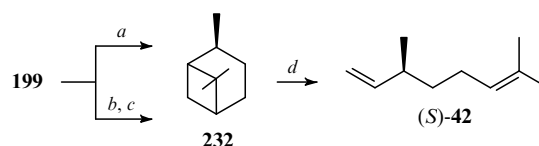


Reagents: (a) hv; (b) NaBH₄; (c) Ac₂O/Py; (d) CrO₃; (e) MeOH/H⁺; (f) MeONa/MeOH; (g) LiAlH₄.

3. Reactions with the opening of both rings

An elegant method for the synthesis of both enantiomers of 2-methyl-6-methylenoocta-2,7-dien-4-ol (ipsdienol) **231**, the aggregation-sex pheromone of many *Ips* species, is based on a four-step transformation of the optically active verbenones **201**. β -Verbenols **230a**–**230d** obtained by the reduction of the corresponding non-conjugated ketones were subjected to flash pyrolysis to give the target alcohols **231** with the retention of the absolute configuration of the chiral centre of C(4) in the corresponding alcohols **230** (Scheme 11).⁵⁶

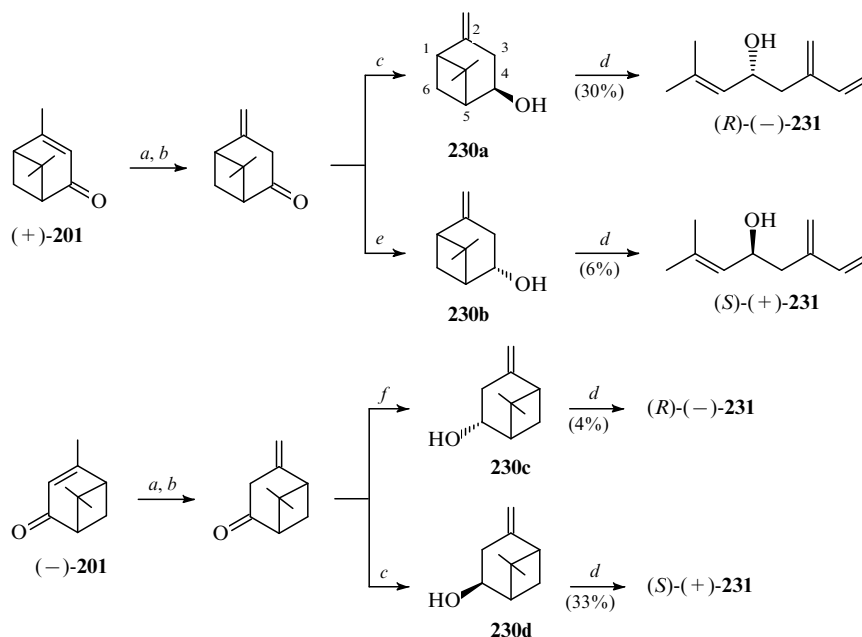
Catalytic hydrogenation of α -(+)-pinene **199** followed by hydroboration and hydrolysis give predominantly *cis*-(+)-pinane **232**.⁵⁷ Its thermolysis yields a mixture of products the main component of which is (*S*)-(+)-dihydromyrcene (*S*)-**42**.⁵⁸



Reagents: (a) H₂/PtO₂ or Ni; (b) B₂H₆; (c) H₂O; (d) 550 °C.

The ketone **233**, the product of the Walker–Tsuji oxidation of the diene (*S*)-**42**, has proved to be a convenient starting material in the synthesis of diprionyl acetate **17** as an equimolar mixture of two diastereomeric pairs having (2*S*,3*S*,7*S*/*R*)- and (2*R*,3*S*,7*S*/*R*)-configurations.⁵⁹ Hydride reduction of the ketone **233** gave a mixture (~1:1) of the *erythro*-(2*S*,3*S*)- and *threo*-(2*R*,3*S*)-alcohols **234** converted into a mixture of diastereomeric diacetoxy alkenes **236** via the corresponding acetates **235**. The latter were obtained in higher yields from the products of allylic oxidation of the ketone **233**. The allylic acetoxy group in **236** was efficiently substituted by alkyl by treatment with the organocuprate reagent. The hydrogenation of the double bond in the thus obtained alkenyl acetate **237** resulting in the formation of the third chiral

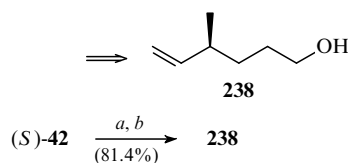
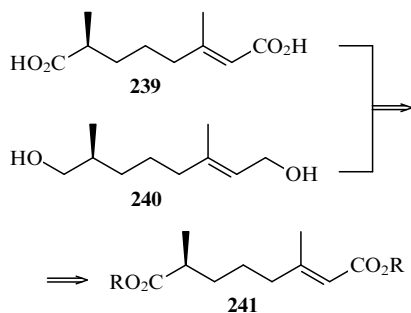
Scheme 11



Reagents: (a) NaH; (b) H₃BO₃; (c) LiAlH₄; (d) 550 °C; (e) (PrⁱO)₃Al/PrⁱOH; (f) Li/NH₃.

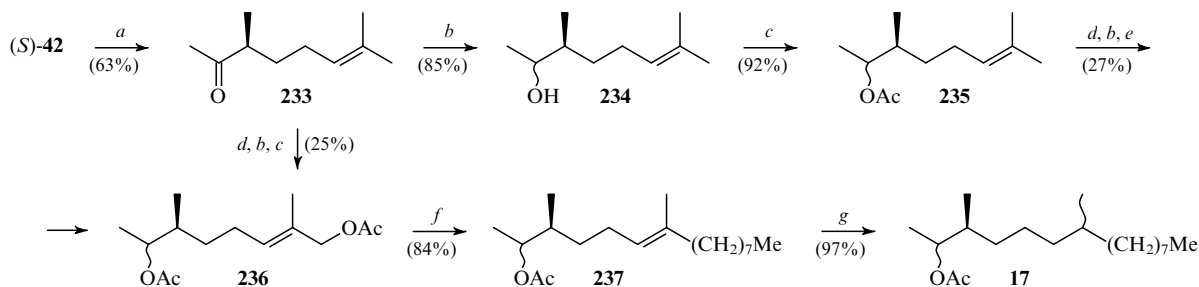
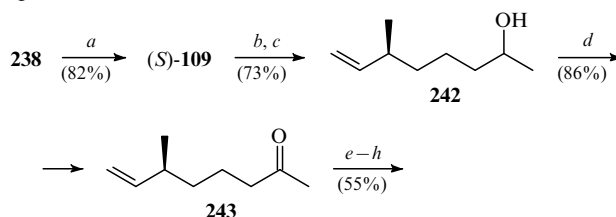
centre at C(7) occurs in a fully nonstereoselective manner (Scheme 12).⁵⁹

The unsaturated alcohol **238**, the product of selective ozonolysis of the diene (*S*)-**42** at the trisubstituted double bond, has been successfully employed in the synthesis of (3,7*S*)-dimethyloct-(2*E*)-enedioic acid **239** and (3,7*S*)-dimethyloct-(2*E*)-ene-1,8-diol **240**, the components of the sex pheromones of the Chinese bean weevil (*Callosobruchus chinensis*) and the African monarch (*Danaus chrysippus*), respectively. A retrosynthetic analysis of **239** and **240** revealed the efficiency of their syntheses *via* the intermediate diester **241**.⁶⁰



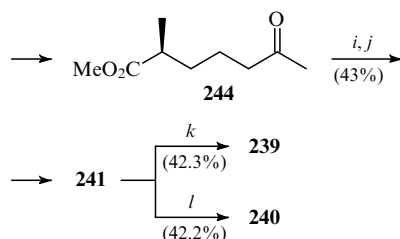
Reagents: (a) O₃/CH₂Cl₂/MeOH; (b) NaBH₄.

To this end, the bromide (*S*)-**109** derived from **238** was introduced into the Grignard reaction with the acetaldehyde; the resulting alcohol **242** was converted into the unsaturated ketone **243** which was further subjected to ozonolysis. The subsequent Horner alkenation of the oxo ester **244** resulted in the diester **241** the hydrolysis or the hydride reduction of which gave the target compounds, **239** and **240**.



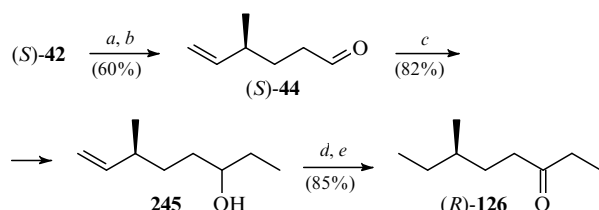
Scheme 12

Reagents: (a) O₂/PdCl₂-CuCl; (b) NaBH₄; (c) Ac₂O/NEt₃/DMAP; (d) SeO₂; (e) Ac₂O/Py; (f) Me(CH₂)₆Br/Mg/CuI; (g) H₂/Pd/C.



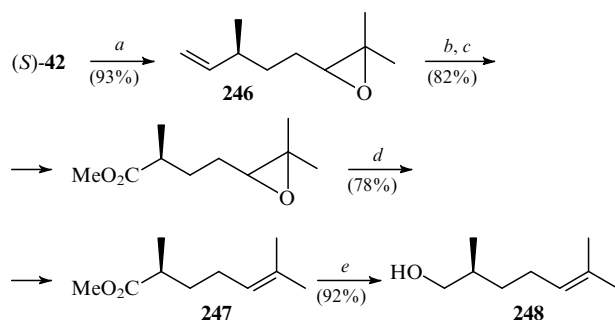
Reagents: (a) PBr_3/Py ; (b) Mg ; (c) MeCHO ; (d) PCC ;
 (e) $\text{O}_3/\text{CH}_2\text{Cl}_2/\text{MeOH}$; (f) $\text{H}_2/\text{Pd}/\text{CaCO}_3-\text{PbO}$; (g) Ag_2O ;
 (h) CH_2N_2 ; (i) $(\text{MeO})_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{Et}/\text{EtONa}$;
 (j) $\text{SiO}_2/\text{AgNO}_3$; (k) NaOH/MeOH ; (l) Bu_2^iAlH .

The aldehyde (S)-44, another product of the ozonolytic cleavage of the diene (S)-42, was used in the synthesis of (6R)-methyloctan-3-one (R)-126, the component of the alarm pheromone of ants of the *Crematogaster* genus.⁶¹ The interaction of the aldehyde (S)-44 with EtMgBr , the catalytic hydrogenation of the double bond in the resulting alcohol 245, and the subsequent oxidation gave the target ketone (R)-126.



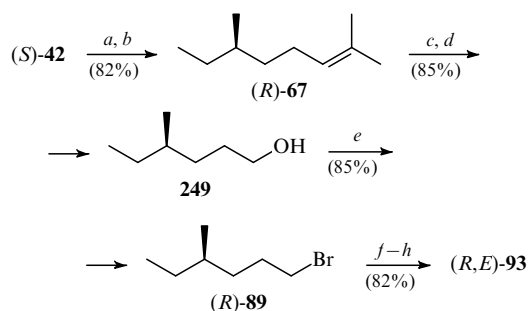
Reagents: (a) $\text{O}_3/\text{CH}_2\text{Cl}_2/\text{MeOH}/\text{NaHCO}_3$; (b) $\text{H}_2/\text{Pd}/\text{CaCO}_3-\text{PbO}$;
 (c) EtMgBr ; (d) $\text{H}_2/\text{Pd}/\text{C}$; (e) PCC .

The synthesis of (2S,6)-dimethylhept-5-en-1-ol 248, the alarm pheromone of ants of the *Acanthomyops claviger* genus,⁶¹ required the scission of the vinyl group in the diene (S)-42. For this purpose, the isopropylidene group, which is more sensitive to electrophilic reagents, was protected by conversion into the epoxide 246. Its ozonolysis followed by regeneration of the double bond with AlI_3 resulted in the ester 247, which was converted into the alcohol 248 by standard procedures.

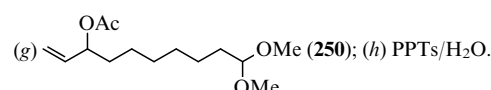


Reagents: (a) $\text{Bu}^t\text{OOH}/\text{Mo}(\text{CO})_6$; (b) $\text{O}_3/\text{CH}_2\text{Cl}_2-\text{MeOH}$;
 (c) $\text{Ac}_2\text{O}/\text{Et}_3\text{N}$; (d) AlI_3/MeCN ; (e) Bu_2^iAlH .

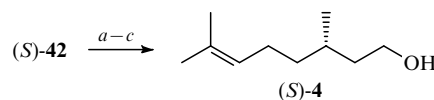
Catalytic hydroalumination of the diene (S)-42 and subsequent hydrolysis gave the alkene (R)-67, which was converted by ozonolysis and reduction into the alcohol 249. The corresponding bromide (R)-89 was used in the synthesis of (R,E)-trogoderma 93.⁶² The regio- and stereo-selective coupling of the magnesium--cuprate reagent derived from (R)-89 with the allylic acetate 250, which occurs as the $\text{S}_{\text{N}}2'$ process, and deprotection gave the target product, (R,E)-93.



Reagents: (a) $\text{Bu}_2^i\text{AlH}/\text{ZrCl}_4$; (b) H_2O ; (c) $\text{O}_3/\text{THF}/\text{MeOH}$; (d) NaBH_4 ;
 (e) PBr_3/Py ; (f) Mg/CuI ;

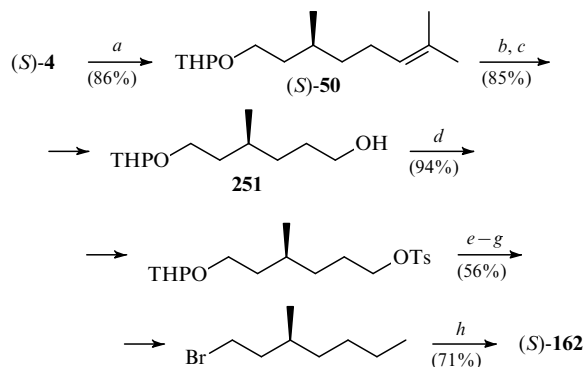


(S)-Citronellol, (S)-4, is the only oxidation product of the organoaluminium adduct of dihydromyrcene (S)-42.⁶³ This compound and some of its derivatives were used in pheromone syntheses



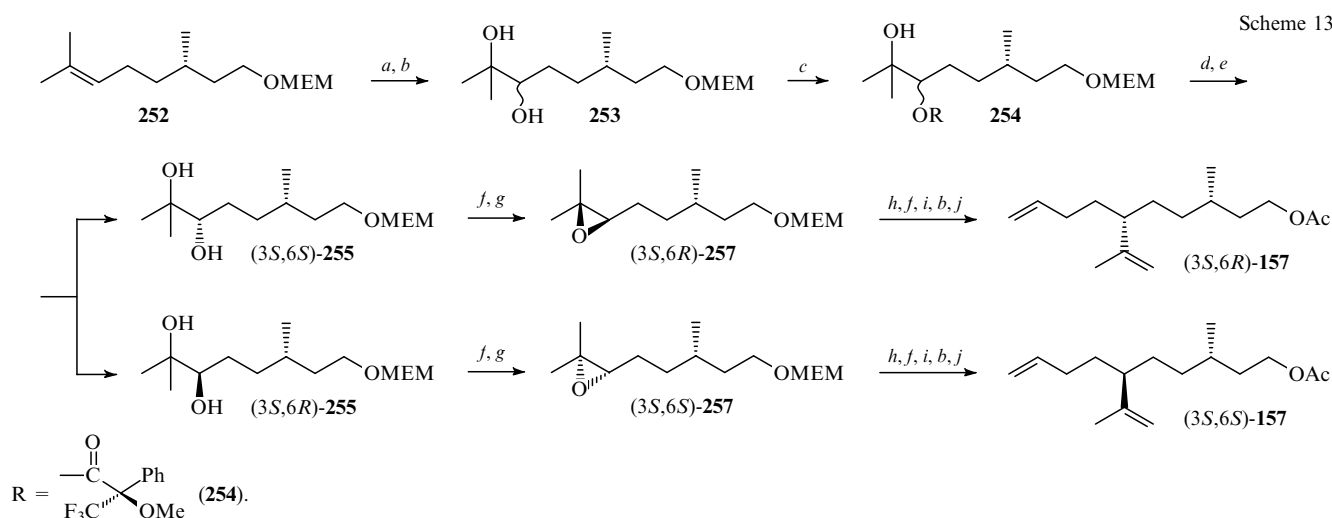
Reagents: (a) Bu_3^iAl or $\text{Bu}_2^i\text{AlH}/\text{ZrCl}_4$; (b) O_2 ; (c) H_2O .

Thus the tetrahydropyranyl ether of (S)-citronellol, (S)-50, has found application in the synthesis of (14S)-methyloctadec-1-ene, (S)-162, after its ozonolytic conversion into the mono-substituted diol 251. Alkylation of the derived tosylate with MeMgI and the subsequent interaction of the bromo-derivative with undec-10-enylmagnesium bromide completed the synthesis of the pheromone (S)-162.⁶³



Reagents: (a) DHP/TsOH ; (b) O_3/MeOH ; (c) NaBH_4 ; (d) TsCl/Py ;
 (e) $\text{MeMgI}/\text{Li}_2\text{CuCl}_4$; (f) $\text{HCl}-\text{H}_2\text{O}$; (g) PBr_3/Py ;
 (h) $\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_9\text{MgBr}/\text{CuI}-2,2'$ -bipyridyl (bipy).

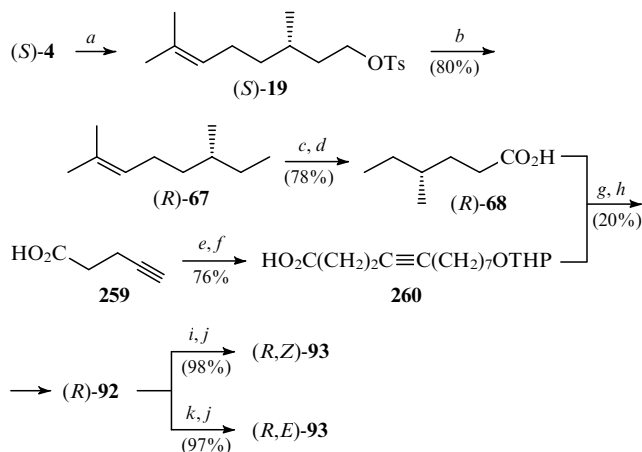
The methoxyethylmethyl ether of citronellol 252 was used in the synthesis of (3S,6R)-157, the pheromone of the California red scale, and its (3S,6S)-enantiomer. For this purpose, compound 252 was converted into the glycol 253 by epoxidation and subsequent hydrolysis; the glycol was treated with (R)-(+)- α -methoxy- α -(trifluoromethyl)phenylacetyl chloride 256 to give the diester 254 as a mixture of diastereomers readily separable chromatographically. Each of these was reduced to the corresponding diol 255; selective mesylation of the secondary hydroxy group and treatment of the mesylates with an alkali gave epoxides 257 with inversion of the chiral centre at the C(6) atom. The



Reagents: (a) MCPBA; (b) H_3O^+ ; (c) RCl (**256**); (d) HPLC; (e) LiAlH_4 ; (f) MeSO_2Cl ; (g) KOH/MeOH ; (h) $(\text{H}_2\text{C}=\text{CHCH}_2\text{CH}_2)_2\text{CuLi}$ (**258**); (i) Bu^nLi ; (j) $\text{Ac}_2\text{O/Py}$.

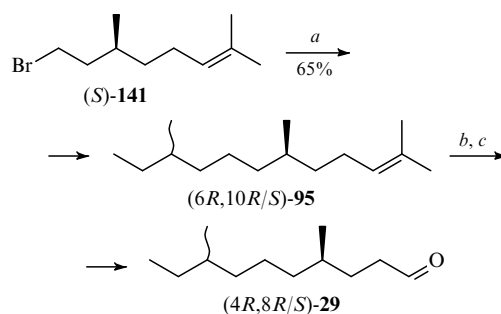
reaction of the epoxide with the cuprate reagent **258**, the dehydration of the intermediate alcohols, and the substitution of the methoxyethylmethyl group for the acetate group completed the synthesis of the pheromone **157** (Scheme 13).⁶⁴

The isomeric trogoderms (*R,E*)- and (*R,Z*)-**93** were synthesised by electrolysis of a mixture of (–)-4*R*-methylhexanoic (*R*)-**68** and 12-(2-tetrahydropyranyloxy)dodec-4-ynoic **260** acids with subsequent stereoselective hydrogenation of the resulting acetylenic alcohol **92**.⁶⁵ The chiral acid (*R*)-**68** was synthesised by ozonolysis and oxidation of the alkene (*R*)-**67**, the product of hydride reduction of citronellyl tosylate (*S*)-**19**, whereas the achiral acid **260**, by alkylation of the pent-4-ynoic acid **259** acetylenide with the bromo ester **94**.



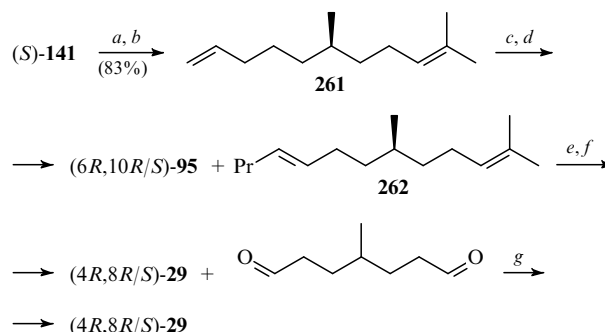
Reagents: (a) TsCl/Py ; (b) LiAlH_4 ; (c) O_3 ; (d) H_2CrO_4 ; (e) Bu^nLi ; (f) **94**; (g) e^- ; (h) HCl ; (i) $\text{H}_2/\text{Pd/CaCO}_3\text{—PbO}$; (j) PCC ; (k) Na/NH_3 .

Citronellyl bromide (*S*)-**141** was used as the starting material in the synthesis of an equimolar mixture of the natural (*4R,8R*)- and the synergistic (*4R,8S*)-enantiomers of the mealworm attractants **29**.⁶⁶ The reaction of the bromide (*S*)-**141** with the Grignard reagent from racemic 1-bromo-2-methylbutane **28** gave the alkene **95**; its ozonolysis and the subsequent reduction of the peroxide completed the synthesis of the pheromone (*4R,8R/S*)-**29**.



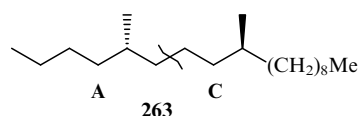
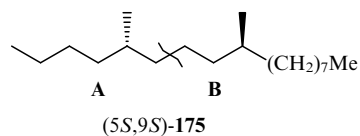
Reagents: (a) **28**/ $\text{Mg/Li}_2\text{CuCl}_4$; (b) $\text{O}_3/\text{MeOH/CH}_2\text{Cl}_2$; (c) Me_2S .

The mixture (*4R,8R/S*)-**29** was obtained in higher yield according to a scheme involving the interaction of the Grignard reagent prepared from the bromide (*S*)-**141** with allyl bromide and selective carbomagnesation of the resulting diene **261** at the terminal double bond.⁶⁶ The carbomagnesation product **95** contained no more than 5% of the diene **262**, which was converted by ozonolysis into the corresponding dialdehyde, which was readily separated from the target product by chromatography.

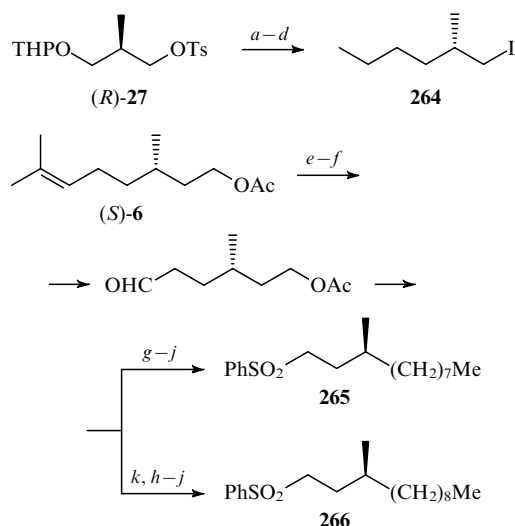


Reagents: (a) Mg ; (b) $\text{H}_2\text{C}=\text{CHCH}_2\text{Br/CuI—bipy}$; (c) $\text{Et}_2\text{Mg/Cp}_2\text{ZrCl}_2$; (d) H_3O^+ ; (e) $\text{O}_3/\text{MeOH—CH}_2\text{Cl}_2$; (f) Me_2S ; (g) SiO_2 .

The sex pheromone of *Leucoptera malifoliella* comprises two components: the major component, (5*S*,9*S*)-dimethylheptadecane **175**, and the minor component, (5*S*,9*S*)-dimethyloctadecane **263**. A retrosynthetic analysis of these compounds shows the expedience of their synthesis from the three chiral blocks: **A**, **B**, and **C**.⁶⁷

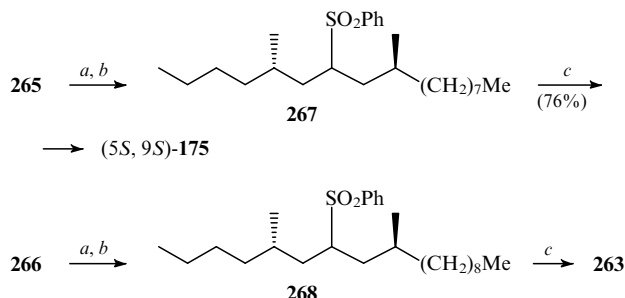


The iodide **264** corresponding to the fragment **A** was synthesised from the tosylate **27**, while the sulfones **265** and **266** corresponding to the blocks **B** and **C**, from (*S*)-citronellyl acetate, (*S*)-**6**.



Reagents: (a) $\text{PrMgBr/Li}_2\text{CuCl}_4$; (b) H_3O^+ ; (c) TsCl/Py ; (d) NaI ; (e) O_3/MeOH ; (f) Me_2S ; (g) $\text{Ph}_3\text{P}=\text{CHBu}$; (h) $\text{LiAlH}_4/\text{CoCl}_2$; (i) PhSNa ; (j) MCPBA ; (k) $\text{Ph}_3\text{P}=\text{CH}(\text{CH}_2)_4\text{Me}$.

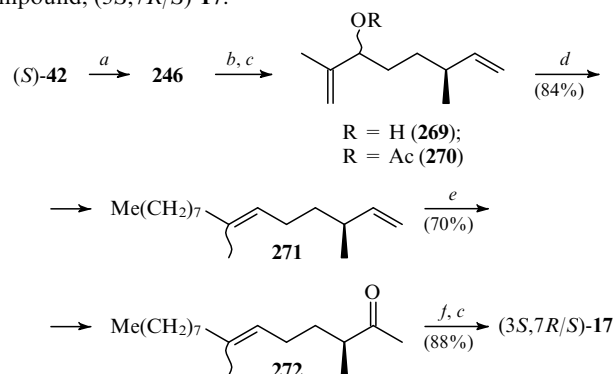
The alkylation of the sulfones **265** and **266** with the iodide **264** and subsequent desulfonation of the products **267** and **268** yielded the target structures, **175** and **263**.



Reagents: (a) Bu^nLi ; (b) **264**; (c) Na-Hg .

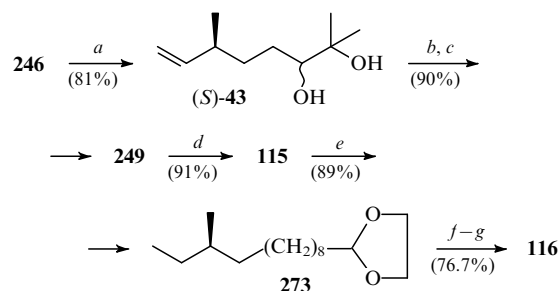
The oxidation of the diene (*S*)-**42** by peroxy acids occurs selectively with the formation of the monoepoxide **246**, which is smoothly isomerised into the allylic alcohol **269** employed in the synthesis of an equimolar mixture of *erythro*- and *threo*-diprionyl acetates **17**, which are configurationally homogeneous with respect to the (3*S*)-chiral centre.⁶⁸ The CuI -catalysed coupling of

the acetate **270** with heptylmagnesium bromide, the conversion of the reaction product **271** into the enone **272** by Walker–Tsuiji oxidation, and further simple conversions yielded the target compound, (3*S*,7*R*)-**17**.



Reagents: (a) MCPBA ; (b) LDA ; (c) $\text{Ac}_2\text{O/Et}_3\text{N/DMAP}$; (d) $\text{Me}(\text{CH}_2)_6\text{MgBr/CuI}$; (e) $\text{O}_2/\text{PdCl}_2-\text{CuCl}$; (f) H_2/Ni .

In the synthesis of (10*R*)-methyl dodecyl acetate **116**, the monoepoxide **246** was converted into the saturated alcohol **249** via the diol (*S*)-**43**. Coupling of the derived tosylate **115** with the Grignard reagent **274** completed the synthesis of the pheromone **116**.⁶⁹

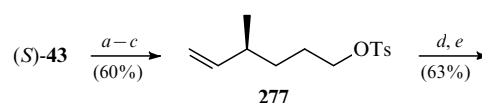


Reagents: (a) HClO_4 ; (b) HIO_4 ; (c) H_2/Ni ; (d) TsCl/Py ;

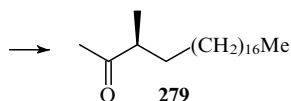
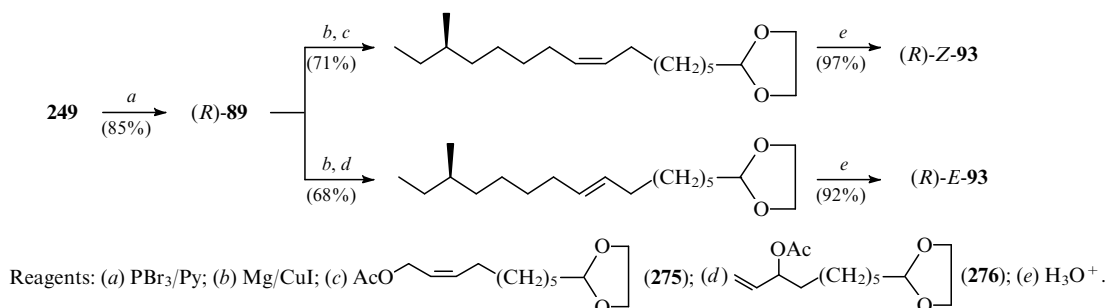
(e) $\text{BrMg}(\text{CH}_2)_5$ (**274**); (f) $\text{HCl}-\text{H}_2\text{O}$;
(g) NaBH_4 ; (h) $\text{Ac}_2\text{O/Py}$.

The bromide (*R*)-**89**, another derivative of the alcohol **249**, was employed in the synthesis of *Z*- and *E*-trogoderms **93** having the (*R*)-configuration. The key stages in this synthesis are the CuI -catalysed cross-couplings of the corresponding Grignard reagent with the primary acetate **275**⁷⁰ and the secondary allylic acetate **276**⁷¹ mediated by the $\text{S}_{\text{N}}2$ and $\text{S}_{\text{N}}2'$ mechanisms, respectively (Scheme 14).

The acid **114** obtained by the Jones oxidation of the diol (*S*)-**43** was used in the synthesis of (+)-(3*S*)-methylheneicosan-2-one **279**, the analogue of the sex pheromone of the German cockroach (*Blattella germanica*). To this end, compound **114** was converted into the tosylate **277** by a two-step procedure; its coupling with the Grignard reagent **278** followed by the Walker–Tsuiji oxidation of the intermediate ketone completed the synthesis of the target ketone **279**.⁷²



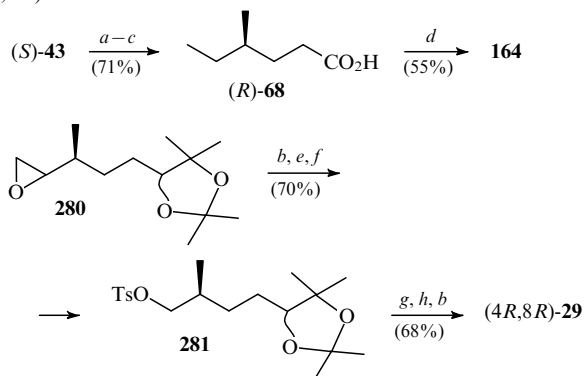
Scheme 14



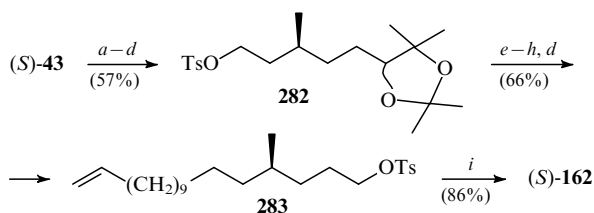
Reagents: (a) H_2CrO_4 ; (b) LiAlH_4 ; (c) TsCl/Py ;
(d) $\text{Me}(\text{CH}_2)_{14}\text{MgBr}$ (**278**)/ Li_2CuCl_4 ; (e) $\text{O}_2/\text{PdCl}_2-\text{CuCl}$.

The diol (*S*)-**43** was used as the starting material in the synthesis of (*4R,8R*)-dimethyldecanal (*4R,8R*)-**29**, another isomer of the mealworm attractant.

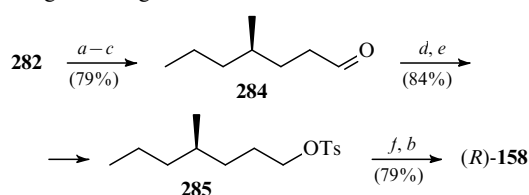
The hydrogenation of the diol (*S*)-**43**, the periodate scission of the intermediate saturated analogue, and the oxidation of the resulting aldehyde with Ag_2O gave the saturated acid (*R*)-**68** further converted into the (*R*)-bromide **164** by the Hunsdiecker reaction. The tosylate **281**, the second component required for the synthesis of (*4R,8R*)-**29**, was synthesised from the epoxide **280**. The Wurtz condensation of compound **281** with the bromide **164** resulted, after a series of simple conversions, in the target product, (*4R,8R*)-**29**.⁷³



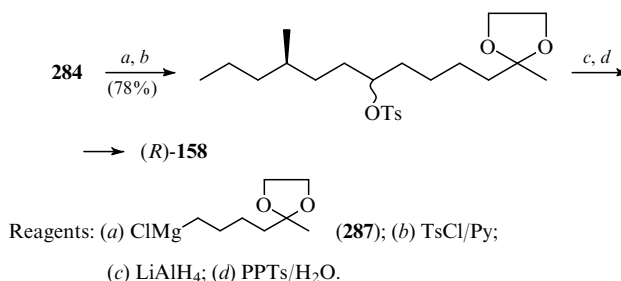
The synthesis of the sex pheromone of the peach leaf mining beetle, (*14S*)-methyloctadec-1-ene (*S*)-**162**, from the diol (*S*)-**43** was based on the successive reactions of the tosylates **282** and **283** with the corresponding Grignard reagents.⁷⁴



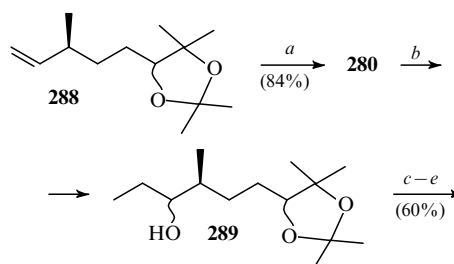
The tosyloxy acetonide **282** has also proved to be a convenient starting material for the synthesis of (*10R*)-methyltridecan-2-one, (*R*)-**158**, which involved the conversion of **282** into the aldehyde **284** and then into the tosylate **285**, which was then coupled with the Grignard reagent **286**.⁷⁵

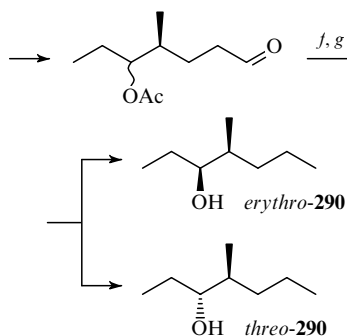


Yet another scheme of synthesis of the pheromone (*R*)-**158** is based on the interaction of the aldehyde **284** with the achiral organomagnesium compound **287**.⁷⁶



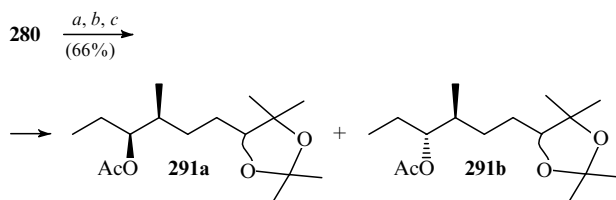
The unsaturated acetonide **288**, which is easily derived from (*S*)-**42**, can be oxidised by peroxy acids into the epoxide **280**, which has been used in the synthesis of 4-methylheptan-3-ol **290**; its (*3S,4S*)-isomer is the aggregation pheromone of the elm engraver (*Scolytus multistriatus*).⁷⁷ The interaction of compound **280** with MeMgI yields the secondary alcohol **289** with a 1 : 1 ratio of the *erythro*- and *threo*-isomers. Further conversions occur without the involvement of the chiral centres. Individual isomers were isolated by HPLC.





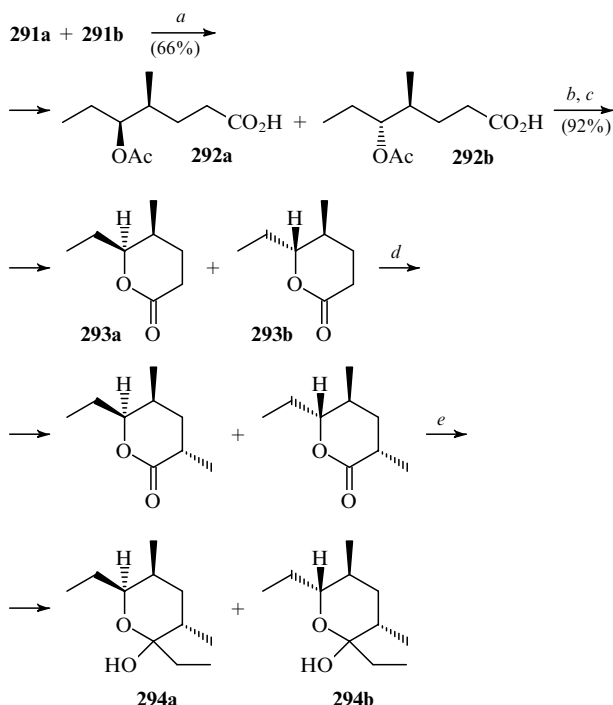
Reagents: (a) MCPBA; (b) MeMgI/CuI; (c) Ac₂O/Py; (d) AcOH–H₂O; (e) HIO₄; (f) NH₂NH₂·H₂O/KOH; (g) HPLC.

The stereoselectivity could be increased up to a ratio of 85 : 15 in favour of the *erythro*-isomer **291a** in the synthesis of (4*S*,6*S*,7*S*)-7-hydroxy-4,6-dimethylnonan-3-one (serricornin) **294a**, the sex pheromone of the tobacco beetle (*Lasioderma serricorne*).⁷⁸



Reagents: (a) HIO₄ (b) EtTi(OPrⁱ)₃; (c) Ac₂O/Et₃N/DMAP.

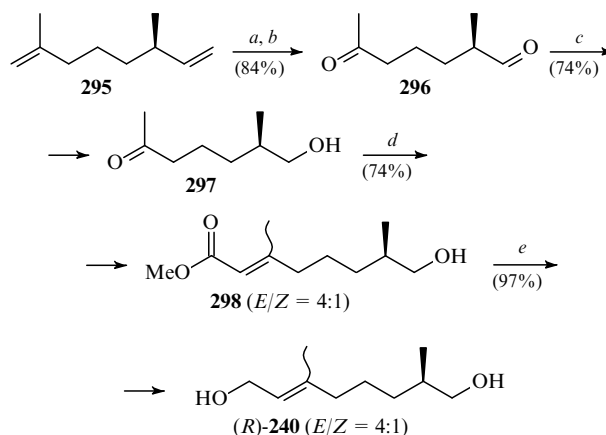
Oxidative cleavage of the dioxolane ring of compounds **291a** and **291b** gave a mixture of *threo*- and *erythro*-acetoxy acids **292a** and **292b**; their alkaline hydrolysis yields a mixture of lactones **293a** and **293b**, which were converted into the target pheromone **294a** containing 15% of the *threo*-isomer **294b**.⁷⁹



Reagents: (a) CrO₃/6N H₂SO₄; (b) KOH/MeOH; (c) HCl/H₂O; (d) MeI, LiN(SiMe₃)₂; (e) EtMgBr.

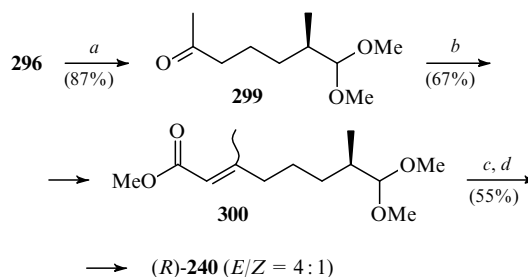
The regioisomers of dihydromyrcene **42**, 2,6-dimethylocta-1,7-dienes **295** of (*R*)- or (*S*)-configuration are the starting chiral building blocks in the synthesis of (*R*)- and (*S*)-enantiomers of 3,7-dimethyloct-(2*E*)-ene-1,8-diols **240** and 3,7-dimethyloct-(2*E*)-ene-

dioic acid **239**, the secretion product of the Monarch butterfly and, correspondingly, of the sex pheromone of *Callosobruchus chinensis*.⁸⁰ The ozonolysis of the diene (*R*)-**295**[†] results in the chiral oxoaldehyde **296**. Its aldehyde carbonyl group was protected either by selective hydride reduction to give the hydroxy ketone **297** or by conversion into the oxo acetal **299** for the subsequent selective alkenation. The Wittig–Horner reaction of the hydroxy ketone **297** with trimethyl phosphonoacetate gave a mixture of isomeric *E*- and *Z*-hydroxy esters **298**. Their reduction yielded a mixture of the corresponding *E*- and *Z*-diols **240** from which the individual *E*-isomer was isolated chromatographically.



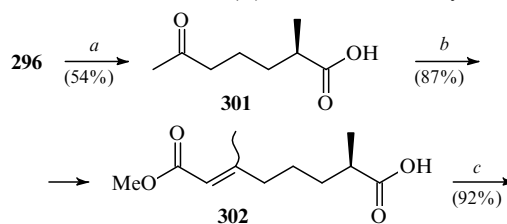
Reagents: (a) O₃; (b) Me₂S; (c) NaBH₄; (d) (MeO)₂P(O)CH₂CO₂Me/NaH; (e) LiAlH₄.

In the second version of this synthesis, the conversion of the oxo acetal **299** into the target diol (*R*)-**240** involved the Wittig–Horner reaction to give a mixture of *E*- and *Z*-esters **300**. Deprotection of the aldehyde function followed by hydride reduction yielded a 4 : 1 mixture of *E*- and *Z*-diols (*R*)-**240**.

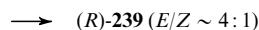


Reagents: (a) MeOH/TsOH; (b) (MeO)₂P(O)CH₂CO₂Me/NaH; (c) NaOH/H₂O; (d) LiAlH₄.

Yet another method of synthesis of the pheromone (*R*)-**239** from the oxo aldehyde **296** has been proposed. This method involved the oxidation of the aldehyde function in the oxo aldehyde **296** and the Wittig–Horner coupling of the oxo acid **301** with trimethyl phosphonoacetate. The resulting mixture of monoesters of the dicarboxylic acids **302** (*E*/*Z* ~ 4 : 1) was hydrolysed and the *E*-isomer of (*R*)-**239** was isolated by HPLC.⁸⁰



[†] The Schemes show the transformations for the (*R*)-enantiomers.



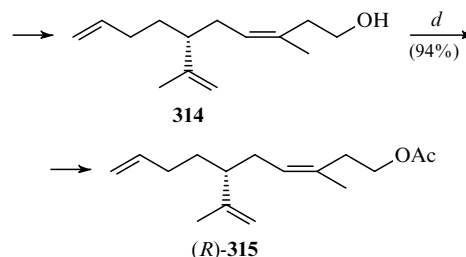
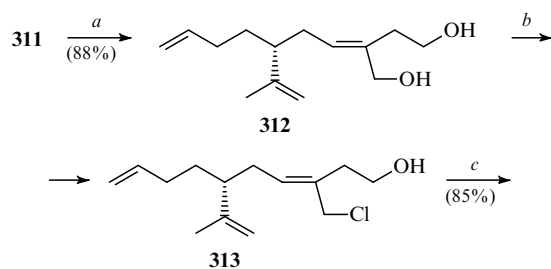
Reagents: (a) AgNO₃/EtOH–H₂O; (b) (MeO)₂P(O)CH₂CO₂Me/NaH;
(c) HCO₂H/H₂O.

IV. Other syntheses

Other monoterpenoid compounds have been used in the synthesis of insect pheromones much more rarely so far. These include alkenes (limonene and dihydrolimonene), alcohols (menthol and linalool),⁸¹ and ketones (menthone, carvone,^{82–85} dihydrocarvone, and camphor).

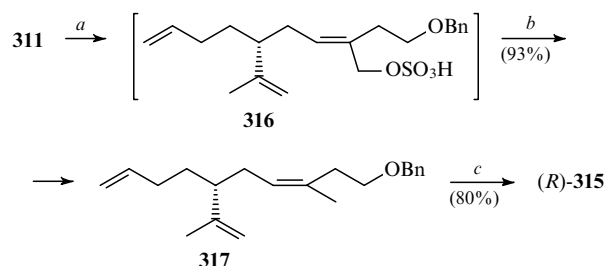
Limonene **303** has proved to be a convenient starting material for the synthesis of pheromones with the isopropenyl group at the chiral centre. The enantiomer (*R*)-**303** was used to synthesise (*6R*)-isopropenyl-3-methyldeca-3,9-dien-1-yl acetate (*R*)-**315**, the sex hormone of the California red scale.⁸⁶ This goal was achieved by partial ozonolysis of (*R*)-**303** which occurred selectively at the endocyclic double bond. The resulting oxo acetal **304** was further converted into the intermediate diethyl phosphate **305**; its treatment with lithium in ammonia gave diene acetal **306**. Deprotection of the carbonyl group and the Peterson condensation of the resulting aldehyde **307** with the silylimine **308** gave the adduct **309**; its hydrolysis gave the conjugated aldehyde **310** further reduced to the allylic alcohol **311** (Scheme 15).

The conversion of the alcohol **311** into the target product, (*R*)-**315**, was carried out in two ways. The first of those involved mild debenzilation under conditions of the Birch reaction, subsequent conversion of the allylic alcohol group of the diol **312** into the allylic chloride, reduction of the chlorohydrin **313**, and acetylation of the alcohol **314**.



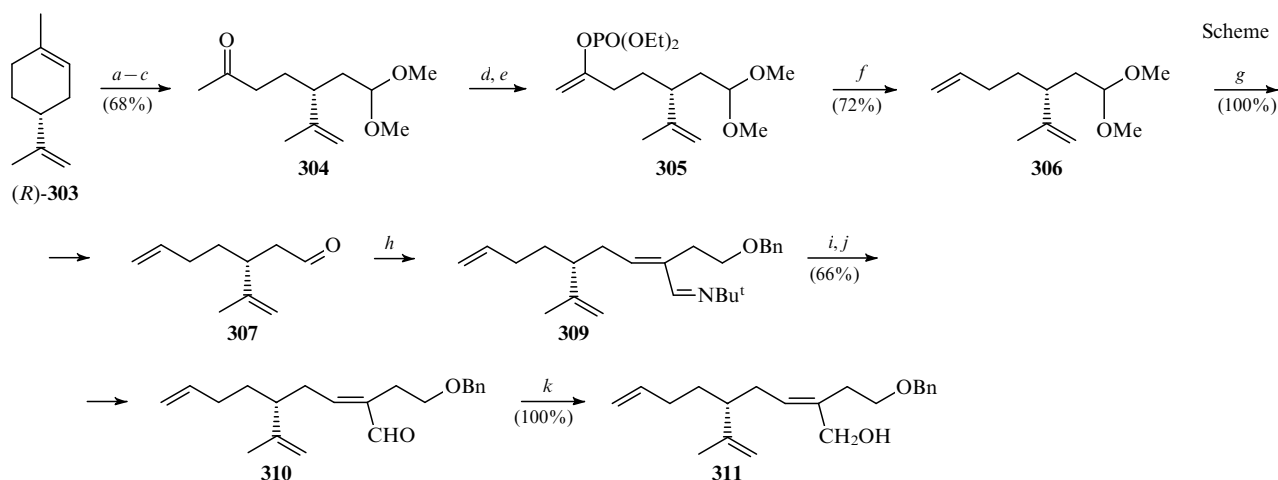
Reagents: (a) Li/NH₃; (b) *N*-chlorosuccinimide (NCS)/Me₂S;
(c) LiAlH₄; (d) Ac₂O/Py.

An alternative way of the transformation of the compound **311** into the acetate (*R*)-**315** involved the synthesis of the sulfonate **316** the reduction of which gave the benzyl ether (**317**). The substitution of the benzyl function in this ether for the acetate yielded the target product, (*R*)-**315**.



Reagents: (a) SO₃/Py; (b) LiAlH₄; (c) Ac₂O/HClO₄.

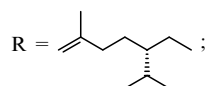
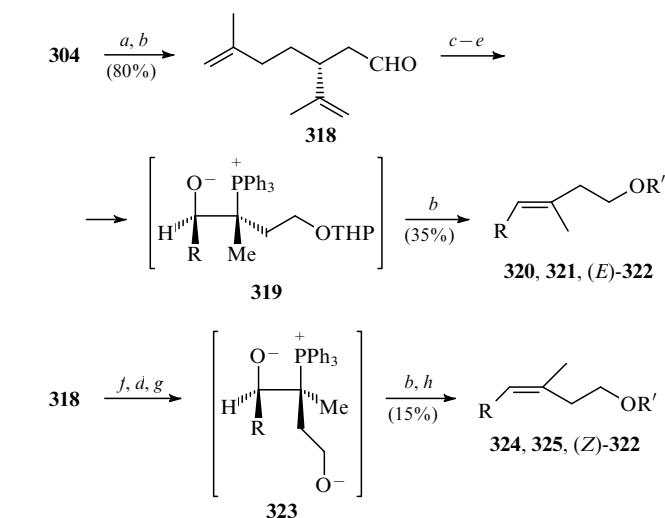
The bifunctional chiral synthon **304** was successfully used in the stereospecific synthesis of (*6R*)-isopropenyl-3,9-dimethyldeca-(3*Z*,9)- and -(3*E*,9)-dien-1-yl propionates **322** of which the *Z*-isomer is the sex pheromone of the white peach scale (*Pseudaulacaspis pentagona*).⁸⁷ In the synthesis of (*E*)-**322**, the dienal **318**, the product of methylenation and subsequent hydrolysis of the oxo acetal **304**, was converted into the trisubstituted intermediate alkene **320** (with the content of the *E*-isomer ≥ 97%) via the intermediate betaine **319** by using a Corey modification of the Wittig reaction. Deprotonation of the betaine formed from MeCH=PPh₃ and the chiral aldehyde **318** and subsequent treatment with ethylene oxide resulted in the *Z*-homoallylic alcohol **324** via the intermediate **323**; the compound **324** was then



Reagents: (a) O₃/MeOH; (b) (NH₂)₂CS; (c) HC(OMe)₃/CeCl₃·6H₂O; (d) LDA; (e) ClPO(OEt)₂; (f) Li/NH₃; (g) HClO₄;

(h) BnOCH₂CH₂CH₂SiEt₂=N^tBu^t (Bn = benzyl) (**308**)/BuⁿLi; (i) (CO₂H)₂/H₂O; (j) PCC; (k) LiAlH₄.

converted into the target component of the pheromone (*Z*)-**322** with the content of the major stereoisomer of $\geq 98\%$.



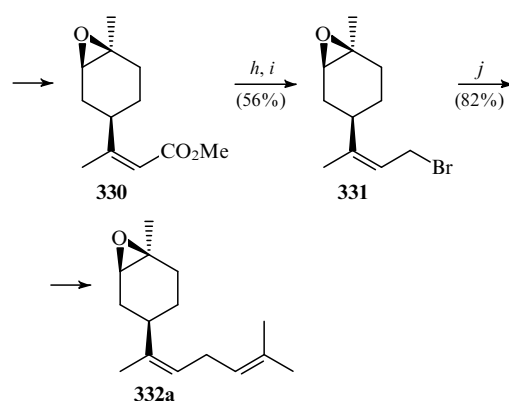
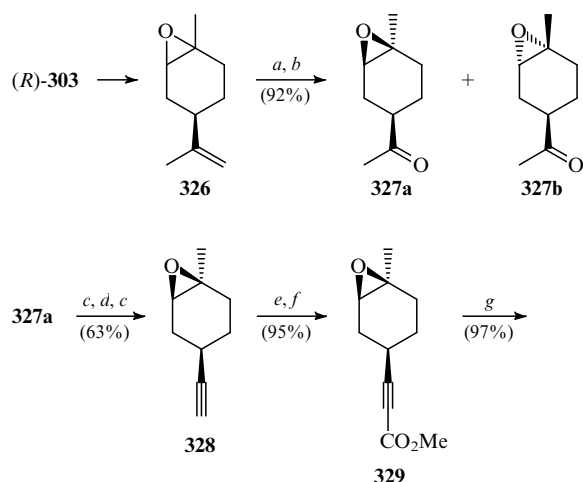
$R' = \text{H (321, 325); THP (320, 324), EtCO [(E)\text{-}322, (Z)\text{-}322].$

Reagents: (a) $\text{Ph}_3\text{P}=\text{CH}_2$; (b) H_3O^+ ; (c) $\text{Ph}_3\text{P}=\text{CH}(\text{CH}_2)_2\text{OTHP}$;

(d) Bu^nLi ; (e) MeI ; (f) $\text{Ph}_3\text{P}=\text{CHMe}$; (g)

(h) $\text{EtCOCl/Et}_3\text{N}$.

A synthetic procedure based on the ozonolysis of a 1:1 mixture of α - and β -limonene epoxides **326** has been proposed for the stereoisomers **332a** and **332b** of the sex pheromone of the green beetle (*Nezara viridula*).⁸⁸ The reduction of the corresponding ozonides yielded a mixture of the ketones **327a** and **327b**, which were separated chromatographically. To obtain the component **322**, the enantiomer **327a** was converted *via* the terminal alkyne **328** into the corresponding ester **329**. The regio- and stereospecific conjugated addition of Me_2CuLi gave the *Z*-alkene **330**, further converted into the bromide **331** *via* the corresponding alcohol. Its condensation with 1-lithio-2-methylpropene resulted in the target product, *endo*-epoxide **332a**.

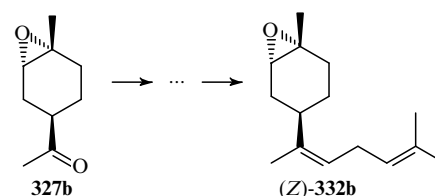


Reagents: (a) O_3 ; (b) PPh_3 ; (c) LDA ; (d) $(\text{EtO})_2\text{P}(\text{O})\text{Cl}$; (e) Bu^nLi ;

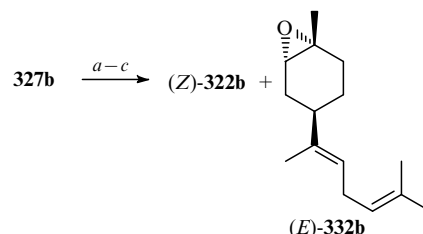
(f) ClCO_2Me ; (g) Me_2CuLi ; (h) Bu_2AlH ; (i) $\text{CBr}_4 \cdot \text{PPh}_3$;

(j) $\text{Br}-\text{CH}(\text{CH}_3)=\text{CH}_2 / \text{Bu}^n\text{Li}$.

The other component, **332b**, was obtained from the ketone **327b** in a similar way.⁸⁸



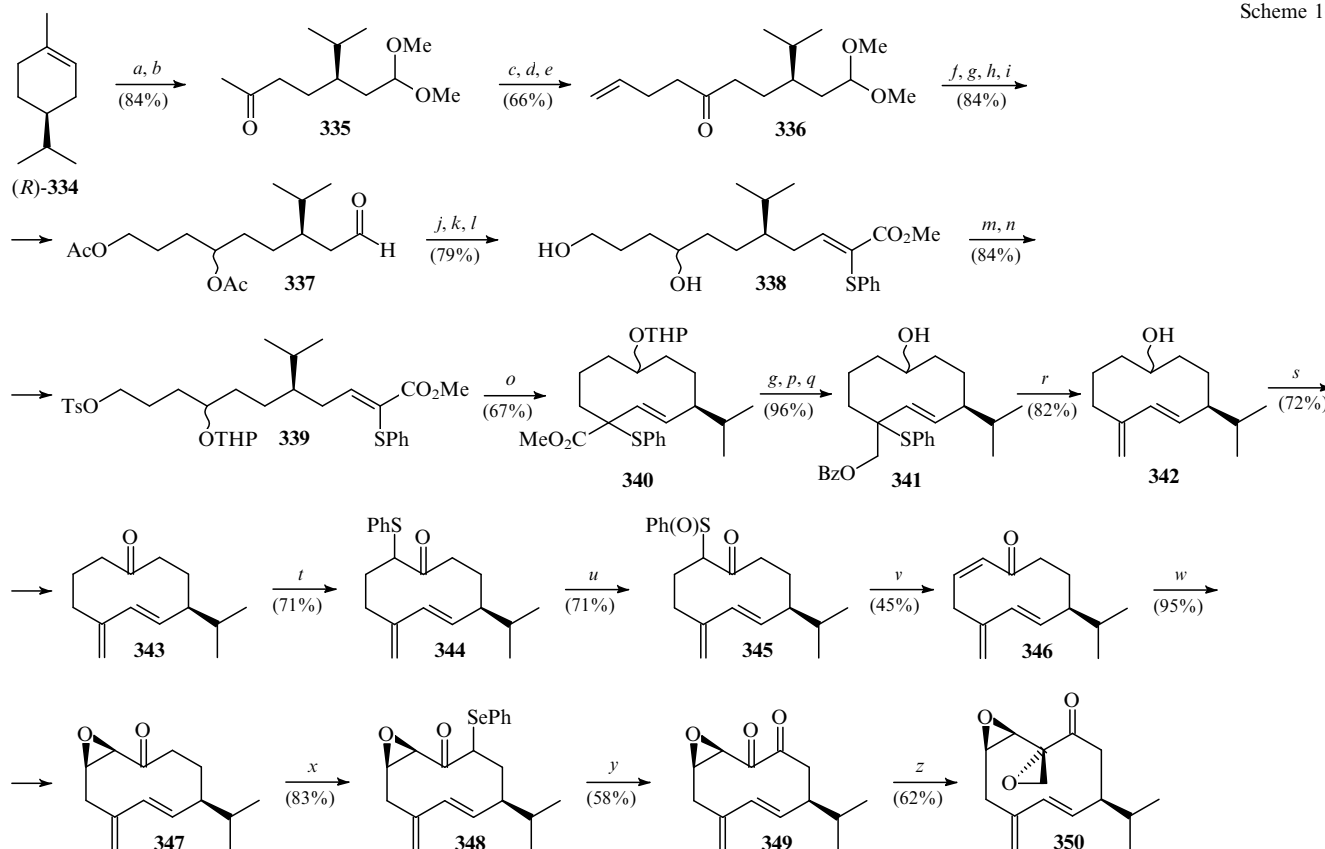
The epoxy ketone **327b** has found application as the starting material in an alternative synthesis of the pheromone **332b**. The coupling of **327b** with the sulfone **333** followed by desulfonation gave a mixture of *Z*- and *E*-isomers of the pheromone **332** from which (*Z*)-**332b** was isolated chromatographically.⁸⁹



Reagents: (a) $\text{PhSO}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ (**333**)/ Bu^nLi ; (b) PhCOCl ; (c) Na-Hg .

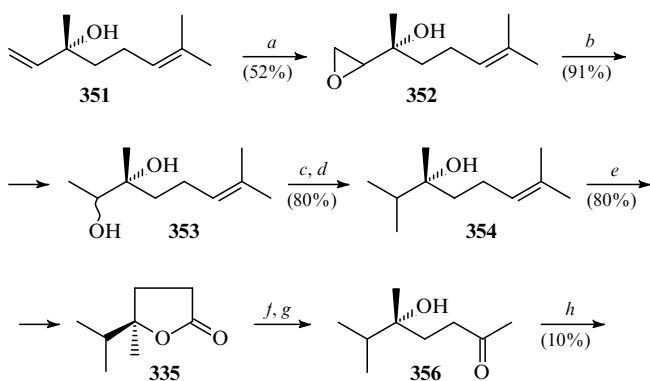
(+)-Dihydrolimonene (*R*)-**334** was used as the starting material in the synthesis of (–)-periplanone B (**350**), the sex pheromone of the American cockroach (*Periplaneta americana*).^{90,91} At the first stage of this synthesis, the terpene (*R*)-**334** was subjected to ozonolysis to give the dimethyl acetal **335**, which was further condensed with allyl bromide. The oxidative cleavage of the double bond in the alkene **336** and the reduction of the intermediate oxo aldehyde gave (after acetylation and deprotection) the aldehyde **337**, which was further converted into the unsaturated dihydroxy sulfide **338**. The tosylation of its primary alcohol group and the protection of the secondary hydroxy group gave compound **339**, which was cyclised upon deprotonation. The product **340** was converted into the sulfoxide by a series of simple reactions; its thermolysis yielded the α,β -unsaturated cyclic ketone **346**. The epoxidation of **346** proceeded regioselectively to give predominantly the epoxide **347**. The latter was converted into the diketone **349** *via* the phenyl selenide **348**; the interaction of **349** with ethylene dimethyl sulfide occurred selectively at one of the oxo groups and gave the target diepoxide **350** (Scheme 16).

Scheme 16



Reagents: (a) O_3/MeOH ; (b) $\text{Me}_2\text{S}/\text{TsOH}$; (c) $(\text{MeO})_2\text{CO}/\text{NaH}$; (d) $\text{H}_2\text{C}=\text{CHCH}_2\text{Br}$; (e) KOH/MeOH ; (f) $\text{OsO}_4-\text{NaIO}_4$; (g) LiAlH_4 ; (h) $\text{Ac}_2\text{O}/\text{Py}$; (i) HCl ; (j) $\text{PhSCH}_2\text{CO}_2\text{Me}/\text{LDA}$; (k) $\text{Ac}_2\text{O}/\text{AcONa}$; (l) $\text{MeONa}-\text{MeOH}$; (m) $\text{TsCl}/\text{Et}_3\text{N}/\text{DMAP}$; (n) DHP/PPTS ; (o) $\text{NaN}(\text{SiMe}_3)_2$; (p) $\text{BzCl}/\text{Py}/\text{DMAP}$; (q) $\text{Dowex } 50\text{W} (\text{H}^+)$; (r) $\text{Na}-\text{C}_{10}\text{H}_8$; (s) PCC/NaOAc ; (t) $\text{PhSSO}_2\text{Ph}/\text{LiN}(\text{SiMe}_3)_2$; (u) NaIO_4 ; (v) $\text{CaCO}_3, 110^\circ\text{C}$; (w) $\text{Bu}^t\text{OOH}/\text{KH}$; (x) $\text{PhSeBr}/\text{LiN}(\text{SiMe}_3)_2$; (y) $\text{H}_2\text{O}_2/\text{Ac}_2\text{O}-\text{AcONa}, \text{K}_2\text{CO}_3$; (z) $\text{Me}_2\text{S}=\text{CH}_2$.

$(R)\text{-}(-)\text{-Linalool}$ (**351**) has found application in the synthesis of the cyclic enol ether, 2-isopropyl-(2*R*),5-dimethyl-2,3-dihydrofuran **357**, the sex pheromone of the female beetles *Hylecoetus dermestoides*. Thus hydroperoxide oxidation of **351** gave the epoxide **352** further reduced to the diol **353**. The selective tosylation of its secondary hydroxy group and the subsequent methylation of the tosylate yielded the alcohol **354**; its oxidation with $\text{RuCl}_3-\text{NaIO}_4$ gave the lactone **355** after spontaneous cyclisation of the intermediate hydroxy acid. The latter was converted into the hydroxy ketone **356**; its cyclisation by distillation over CaSO_4 completed the synthesis of the pheromone **357**.⁹²

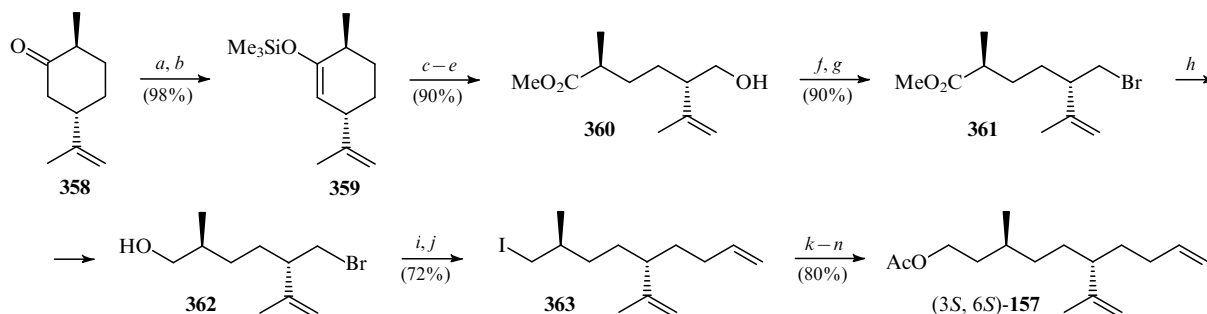


$(R)\text{-}357$
 Reagents: (a) $\text{Bu}^t\text{OOH}/\text{VO}(\text{acac})_2$; (b) LiAlH_4 ; (c) TsCl/Py ; (d) $\text{Me}_2\text{Cu}(\text{CN})\text{Li}_2$; (e) $\text{RuCl}_3/\text{NaIO}_4$; (f) LiOH ; (g) LiMe ; (h) distillation over CaSO_4 .

$(-)\text{-Dihydrocarvone}$ **358** was used in the synthesis of (3*S*,6*S*)-**157**, the component of the sex pheromone of the California red scale.⁹³ To this end, the ketone **358** was converted into the enol silyl ether **359**; its ozonolysis gave the hydroxy ester **360**. The latter was converted into the target product, (3*S*,6*S*)-**157** via the bromo ester **361**, bromohydrin **362**, iodide **363**, and the corresponding nitrile (Scheme 17).

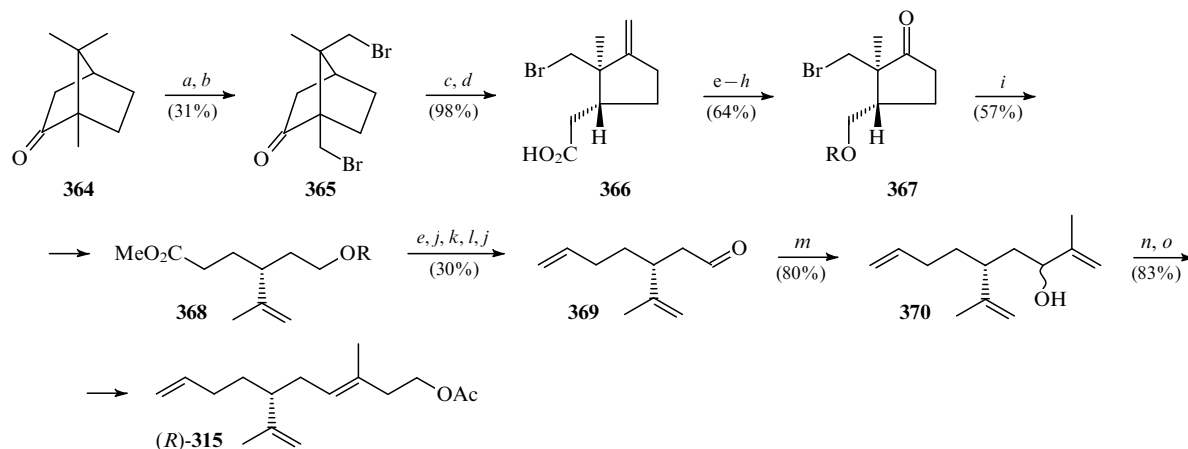
Another component of the sex pheromone of the California red scale, $(R)\text{-}315$, has been synthesised from (+)-camphor **364** taking advantage of possible cleavage of its 9,10-dibromo-derivative **365** under alkaline conditions to give the unsaturated bromo acid **366** which was converted into the β -bromo-ketone **367** by a series of simple reactions. Its treatment with NaOMe gave the acyclic hydroxy ester derivative **368**. The latter was transformed into the aldehyde **369** the condensation of which with 2-propenylmagnesium bromide gave the allylic alcohol **370**. Its stannyl derivative underwent a highly stereoselective 2,3-sigmatropic rearrangement into the corresponding homoallylic alcohol (Scheme 18).⁹⁴

Scheme 17



Reagents: (a) LDA; (b) Me₃SiCl; (c) O₃/MeOH/CH₂Cl₂; (d) NaBH₄; (e) CH₂N₂; (f) MsCl/Py; (g) Bu₄NBr; (h) Bu₂AlH; (i) H₂C=CHCH₂MgCl/CuI; (j) I₂·PPh₃; (k) NaCN; (l) NaOH; (m) LiAlH₄; (n) Ac₂O/Py.

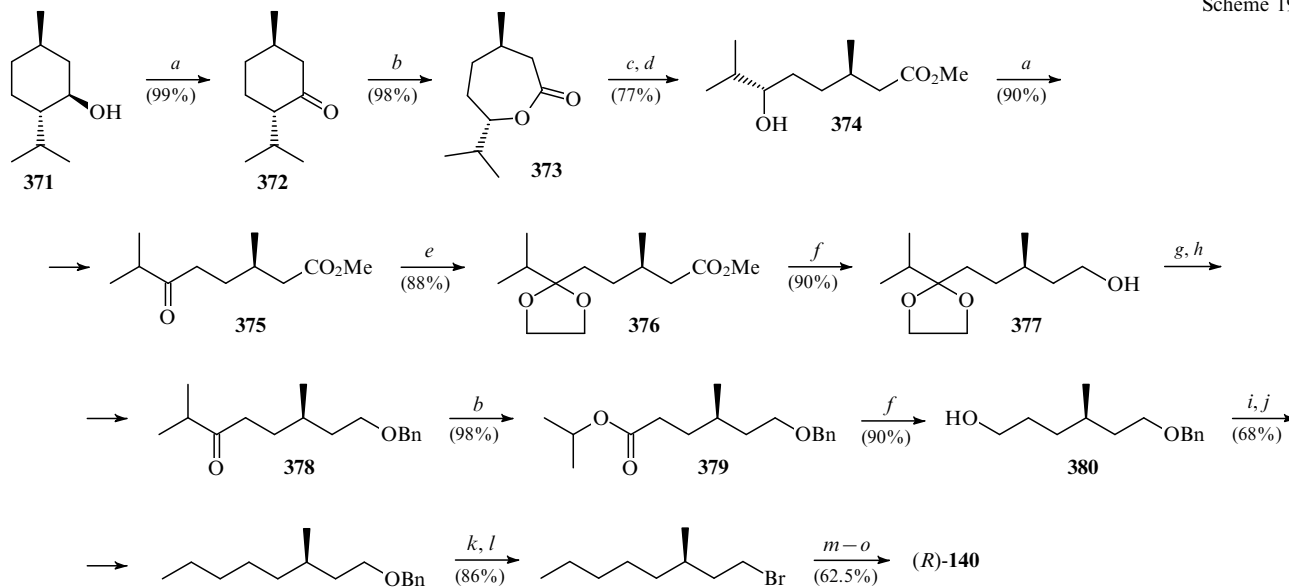
Scheme 18



R = Bu^tMe₂Si.

Reagents: (a) Br₂/ClSO₃H; (b) Zn/NaOH; (c) KOH/DMSO; (d) HCl; (e) LiAlH₄; (f) O₃/MeOH; (g) Me₂S; (h) Bu^tMe₂SiCl/DMAP; (i) NaOMe; (j) PCC; (k) H₂C=PPh₃; (l) Bu₄NF; (m) CH₂=C(Me)MgBr; (n) Bu₃SnCH₂I/BuⁿLi; (o) Ac₂O/Py.

Scheme 19

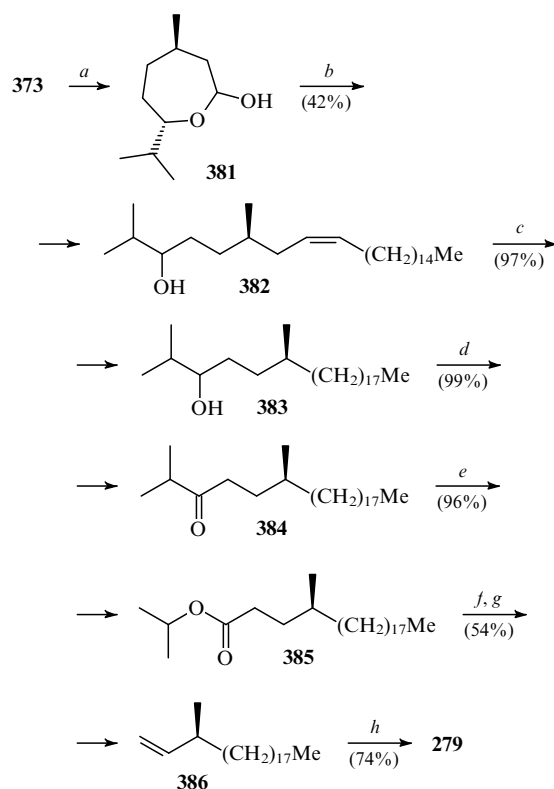


Reagents: (a) PCC; (b) C₁₀H₂₁SO₃H; (c) KOH/MeOH; (d) MeOH/TsOH; (e) (CH₂OH)₂/TsOH; (f) Bu₂AlH; (g) BnCl/KOH; (h) HCl; (i) TsCl/Py; (j) Et₂CuLi; (k) H₂/PdCl₂; (l) PBr₃/Py; (m) Mg; (n) CO₂; (o) LiAlH₄.

(3*R*,7)-Dimethyloctan-(6*S*)-olide **373**, the product of regio- and stereo-specific Baeyer–Williger oxidation of (–)-menthone **372** derived from L-(–)-menthol **371** is especially promising in the synthesis of the enantiomerically pure insect pheromones.

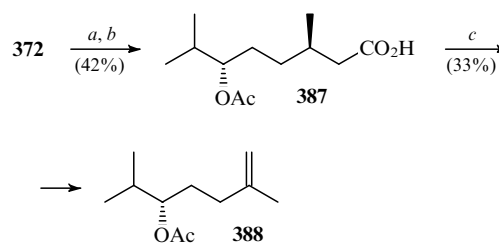
The synthesis of the pheromone of the mealworm, (*R*)-**140**, from the key lactone **373** involved the preparation of benzyloxy ketone **378** after a series of simple unambiguous transformations of the compound **374** into the compound **377**; its conversion into the target product involved the formation of the isopropyl ester **379** and the monobenzyl derivative of the diol **380** (Scheme 19).^{95,96}

To obtain the optically pure analogue of the sex pheromone of the German cockroach **279**, the lactone **373** was reduced into the corresponding lactol **381**; its alkenation and hydrogenation of the resulting *Z*-alkene **382** gave the alcohol **383**. The further modification of its hydrocarbon skeleton to that of the target compound, α -methyl ketone **279**, involved the sequence of conversions which did not affect the chiral centre at C(6): viz., the oxidation of **383** to the ketone **384**, which underwent regiospecific Baeyer–Williger oxidation into the isopropyl ester **385** and the oxidative decarboxylation of the corresponding acid and Walker–Tsuiji oxidation of the resulting alkene **386**.^{97,98}



Reagents: (a) Bu_2AlH , -75°C ; (b) $[\text{Me}(\text{CH}_2)_{14}\text{P}^+\text{Ph}_3]\text{Br}^-/\text{Bu}^n\text{Li}$; (c) H_2/Ni ; (d) PCC; (e) MCPBA; (f) KOH/MeOH ; (g) $\text{Pb}(\text{OAc})_4/\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$; (h) $\text{O}_2/\text{PdCl}_2-\text{CuCl}$.

The synthesis of (3*S*)-acetoxy-2,6-dimethylhept-6-ene **388**, the analogue of the Comstock's scale (*Pseudococcus comstocki*) pheromone, is also based on the Baeyer–Williger oxidation of the original ketone **372** and subsequent oxidative decarboxylation of the intermediate acetoxy acid **387**.⁹⁹



Reagents: (a) $\text{AcOOH}/\text{H}_2\text{SO}_4$; (b) $\text{Ac}_2\text{O}/\text{Py}$; (c) $\text{Pb}(\text{OAc})_4/\text{Cu}(\text{OAc})_2$.

The present review clearly demonstrates the efficiency of application of optically active monoterpenoids in the syntheses of chiral insect pheromones.

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Carborane-containing organophosphorus compounds. Synthesis and properties

N N Godovikov, V P Balema, E G Rys

Contents

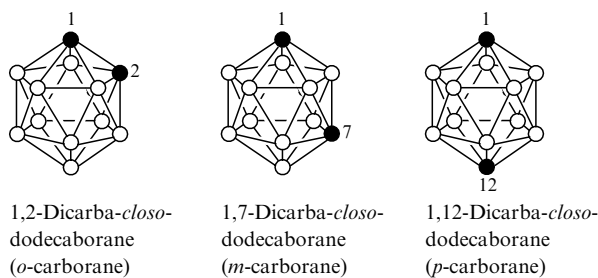
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Abstract. Published data on the synthesis, chemical properties and practical use of carborane-containing organophosphorus compounds are surveyed. Their properties are compared with those of similar organophosphorus derivatives devoid of carboranyl groups. The bibliography includes 89 references.

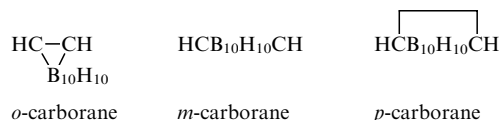
I. Introduction

Carborane-containing organophosphorus derivatives constitute an interesting class of compounds that has been insufficiently investigated.

Although a large number of studies devoted to these substances have been published, these publications are not systematic, and this does not make it possible to estimate adequately the influence of carboranyl and phosphorus-containing fragments on the reactivity of these derivatives. In this review, we generalise and describe systematically the published data dealing with carborane-containing organophosphorus derivatives; our consideration has been restricted to dicarba-*closo*-dodecaborane derivatives. The structures and the numbering of atoms in 1,2-, 1,7- and 1,12-dicarba-*closo*-dodecaboranes are presented below.



These isomers are usually represented using the following brief symbols:



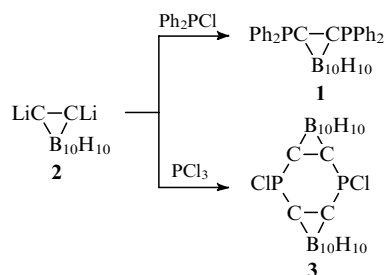
We consider methods for the synthesis of carborane-containing derivatives of trivalent and pentavalent phosphorus and discuss their chemical properties and their potential applications.

II. Carborane-containing derivatives of trivalent phosphorus

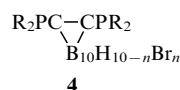
1. Carboranylphosphines

a. Synthesis of carboranylphosphines

The first representative of carboranylphosphines, namely, bis(diphenylphosphino)-*o*-carborane **1** was synthesised in 1963 by the reaction of dilithio-*o*-carborane **2** with chlorodiphenylphosphine.^{1–3} Subsequently, reactions of lithiocarboranes with trivalent phosphorus acid chlorides have been widely used to prepare various carborane-containing organophosphorus compounds including those with cyclic structures like compound **3**.³



Reactions of the compound **2** and dilithio-derivatives of *B*-bromo-*o*-carborane with chlorodiphenylphosphine⁴ and chlorodiethylphosphine⁵ gave rise to the corresponding bis-phosphines **4**:



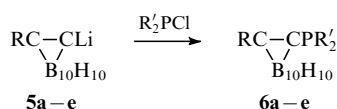
R = Et, Ph; *n* = 0, 1.

Monolithiocarboranes **5** substituted at the 1-position have also been introduced into the reactions with chlorophosphines.^{5–7}

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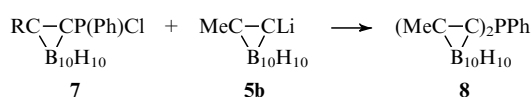
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Uspekhi Khimii **66** (12) 1125–1140 (1997); translated by Z P Bobkova



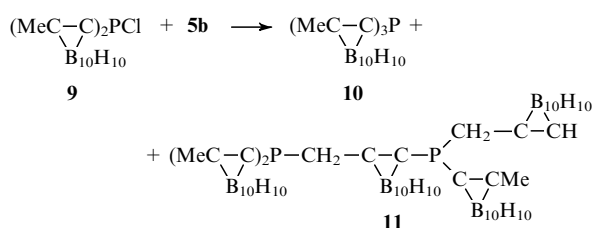
R = H (**a**), Me (**b**), Ph (**c**), HC=CH₂ (**d**), MeC=CH₂ (**e**);
R' = Me, Et, Ph.

Bis- and tris-carboranylphosphines have been prepared in a similar way; for this purpose, the lithiocarborane **5b** was made to react with carboranylchlorophosphines. Chloro(2-methyl-*o*-carboranyl)phenylphosphine **7** (R = Me) was converted in this way into bis(2-methyl-*o*-carboranyl)phenylphosphine **8**.⁷

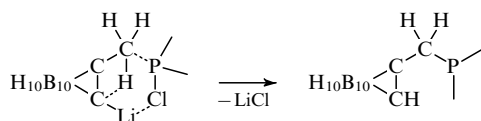


R = Me, Ph.

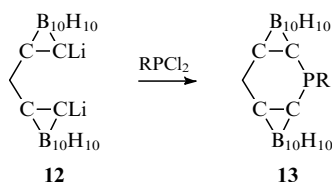
At the same time, chloro(2-phenyl-*o*-carboranyl)phenylphosphine **7** (R = Ph) does not enter into this reaction. This was attributed⁷ to both steric and electronic influences of the substituent at the second carbon atom of the carborane nucleus. It is of interest that the reaction of chlorobis(2-methyl-*o*-carboranyl)phosphine **9** with the lithio-derivative **5b**, in addition to tris(2-methyl-*o*-carboranyl)phosphine **10**, has given a complex penta-carboranyl compound **11**, the structure of which has been confirmed by X-ray diffraction analysis.⁸



The formation of the abnormal reaction product **11** was explained⁸ by the occurrence of a number of processes including either metallation of a methyl group in chlorobis(methyl-*o*-carboranyl)phosphine **9** and disproportionation of the resulting carboranymethylolithium or transfer of the reaction site in the lithio-derivative **5b** from the carbon atom linked to lithium to the carbon atom of the methyl group *via* a six-centred transition state.⁸



A number of cyclic *o*-carboranylphosphines have been described. For example, phosphines **13** containing a phosphinane ring have been obtained by the reaction of bis(lithiocarboranyl)methane **12** with MePCl₂ or PhPCl₂.⁹

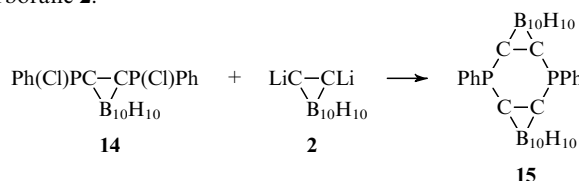


R = Me, Ph.

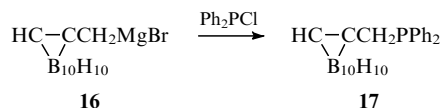
According to X-ray diffraction analysis, the C–P–C angle in the six-membered ring in the methyl derivative **13** (R = Me) differs only slightly from its normal value, whereas the C–CH₂–C angle is markedly larger than the tetrahedral angle and is equal to 121.8°.¹⁰

Phosphine **15** having a similar structure but containing two phosphorus atoms in the ring has been prepared by treatment of

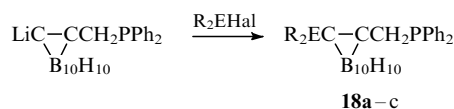
1,2-bis(chlorophenylphosphino)-*o*-carborane **14** with the dilithiocarborane **2**.³



Synthesis of carboranylphosphines in which the phosphorus atom is separated from the carboranyl nucleus by methylene groups has been reported. Thus the reaction of *o*-carboranymethylmagnesium bromide **16** with chlorodiphenylphosphine has given rise to (*o*-carboranymethyl)diphenylphosphine **17**.¹¹

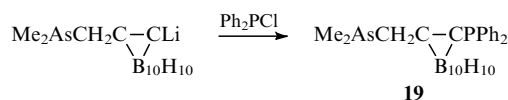


The compound **11** mentioned above belongs to the same type of derivative. 1,2-Disubstituted *o*-carboranes **18** containing a dimethylphosphino, diphenylphosphino or dimethylarsino group, in addition to the diphenylphosphinomethyl group, have been obtained by treatment of the lithio-derivative of the phosphine **17** with chlorodimethylphosphine, chlorodiphenylphosphine or iododimethylarsine, respectively.¹²

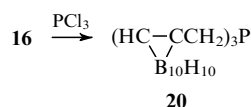


R = Me, E = P (**a**); R = Ph, E = P (**b**); R = Me, E = As (**c**);
Hal = Cl, I.

1-Diphenylphosphino-2-dimethylarsinomethyl-*o*-carborane **19** was prepared by the reaction of chlorodiphenylphosphine with the lithio-derivative of the corresponding carborane.

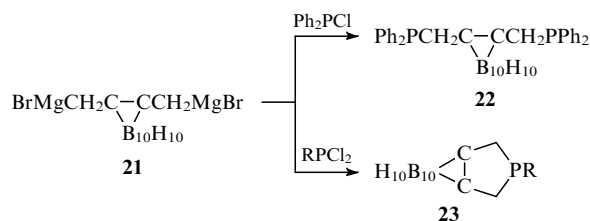


The reaction of *o*-carboranymethylmagnesium bromide **15** with PCl₃ yields tris(*o*-carboranymethyl)phosphine **20**.¹³



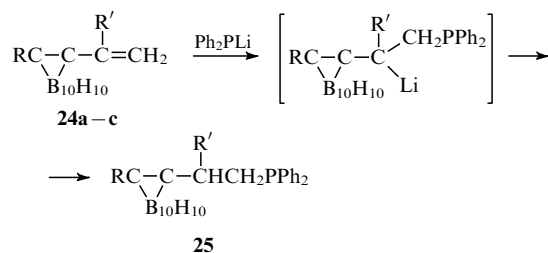
Treatment of bis(bromomagnesiomethyl)-*o*-carborane **21** with Ph₂PCl has resulted in the synthesis of 1,2-bis(diphenylphosphinomethyl)-*o*-carborane **22**.¹²

The reaction of **21** with MePCl₂ or PhPCl₂ affords the corresponding phospholanes **23**.⁶



R = Me, Ph.

Carboranylphosphines **25** in which the phosphorus atom is separated from the carboranyl nucleus by two carbon atoms have been synthesised by nucleophilic addition of Ph₂PLi to the double bonds in 1-vinyl- and 1-isopropenyl-2-substituted carboranes **24**, activated by the presence of the *o*-carboranyl substituent, in a boiling ether–benzene mixture.¹⁴



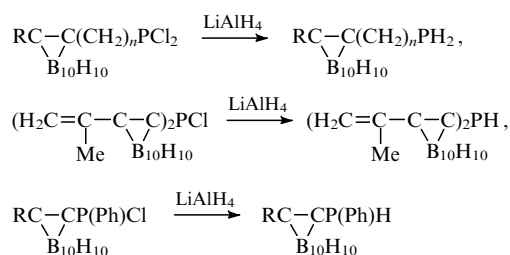
R = Me, R' = H (a); R = R' = Me (b); R = MeC=CH₂, R' = Me (c).

The resulting phosphines are difficultly crystallisable viscous substances, which have been isolated after treatment with MeI as the corresponding phosphonium salts.

The activation of the double bond in 1-vinyl- and 1-isopropenyl-2-substituted *o*-carboranes **24a–c** towards nucleophilic addition is due to the high electron-withdrawing ability of the *o*-carborane nucleus. In the case of 1,2-diisopropenyl-*o*-carborane **24c**, Ph₂PLi adds only to one double bond. This is due to the fact that the negative charge arising upon the addition of a Ph₂PLi molecule decreases the electronegativity of the carboranyl fragment and thus prevents the reaction at the second isopropenyl group.

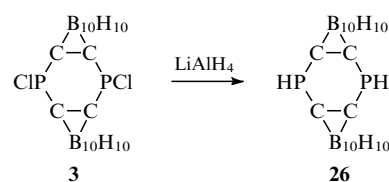
For the same reason, a similar derivative of *m*-carborane does not react with Ph₂PLi at all;¹⁴ in fact, *m*-carboranyl is a weaker electron-withdrawing group than *o*-carboranyl.

Synthesis of *o*-carboranylphosphines containing a PH group has required a totally different approach. These compounds have been obtained in 50%–70% yields by reduction of the corresponding chlorophosphines with LiAlH₄ in ether.^{7,11} However, the attempt to reduce chlorobis(2-phenyl-*o*-carboranyl)phosphine failed.



R = Me, Ph; n = 0, 1.

The reduction of the cyclic dichlorophosphine **3** with LiAlH₄ in ether gives diphosphine **26** in 60% yield.⁷

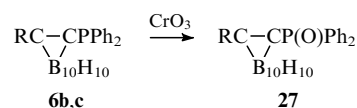


It should be noted that the use of an excess of LiAlH₄ in the reduction of carboranylchlorophosphines leads to the cleavage of the C–P bond giving the corresponding carborane and phosphine. However, in the case of carboranyl(chloro)phenylphosphines, this reaction pathway was not observed.⁷ This indicates that a Ph group at the phosphorus atom increases the stability of the phosphorus–carboranyl carbon bond with respect to nucleophiles.

b. Properties of carboranylphosphines

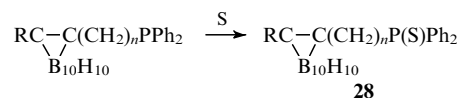
All the main properties of phosphines containing no carboranyl groups are also characteristic of carboranylphosphines. At the same time, carboranyl groups have a certain influence on the properties of the phosphine group. This effect depends on the number of carboranyl groups and on their structure and also on the nature of substituents in the carborane nucleus and at the phosphorus atom. In the majority of cases, it is difficult to determine whether electronic or steric factors exert the major influence.

Carboranylphosphines are stable with respect to atmospheric oxygen. They are oxidised under relatively drastic conditions. For example, oxidation of methyl- and phenyl-substituted *o*-carboranylphosphines **6b,c** to the corresponding phosphine oxides **27** has been accomplished only by treating them with CrO₃ in acetic acid.¹¹



R = Me, Ph.

The addition of sulfur to tertiary carboranylphosphines occurs with greater difficulty than its addition to ordinary tertiary phosphines, the reaction conditions being dependent both on the substituents in the carborane nucleus and on the distance between this nucleus and the phosphorus atom.¹¹

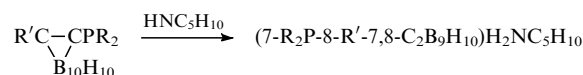


n = 1, R = H (**17**); n = 0, R = CH=CH₂ (**6d**);

n = 0, R = MeC=CH₂ (**6e**).

Whereas (*o*-carboranymethyl)diphenylphosphine **17** enters into this reaction under mild conditions, namely, in benzene at 60 °C, the same reaction involving the carboranylphosphines **6d** and **6e** requires heating to 180 °C.¹¹

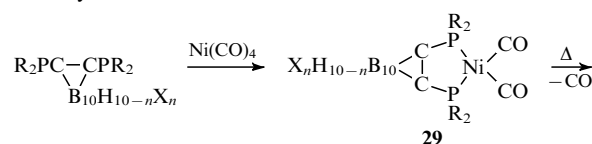
In an alkaline medium, carboranylphosphines are easily cleaved at the P–C(carborane) bond; however, on treatment with pyridine under mild conditions, this bond is retained. In this case, the carborane nucleus is opened to give *nido*-carboranylphosphines.¹⁵

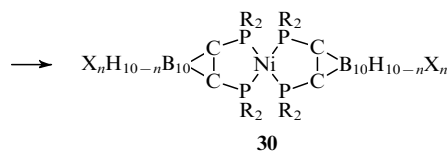


R = Ph, Et, Prⁱ, OEt; R' = Me, PR₂.

c. Transition metal complexes with carboranylphosphines

Soon after the first carboranylphosphines had been obtained, publications dealing with their use as ligands in transition metal complexes appeared. The first carboranylphosphine complexes of nickel, namely, dicarbonyl-1,2-bis(diphenylphosphino)- and -1,2-bis(diethylphosphino)-*o*-carboranylnickel **29** (R = Et, Ph, X = H), were obtained from the corresponding carboranyldiphosphines and Ni(CO)₄ in chloroform or in hydrocarbon solvents at 20 °C.³ Dicarbonyl-1,2-bis(diethylphosphino)-*o*-halocarboranylnickel complexes **29** (R = Ph, X = Cl, Br) are prepared in a similar way under mild conditions.¹⁶



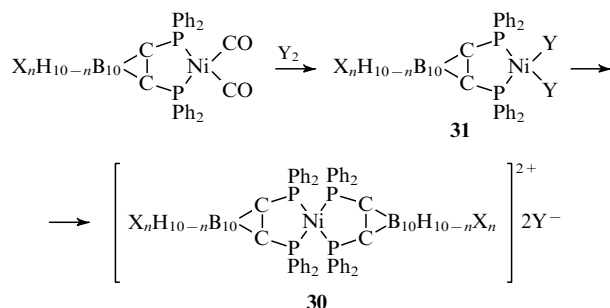


$n = 1-3$; $R = \text{Et, Ph}$; $X = \text{H, Cl, Br}$.

Study of the IR spectra of the complexes **29** shows that the characteristic CO frequencies are markedly greater than those for other complexes of the same type [for example, *o*-(Ph₂P)₂C₆H₄Ni(CO)₂ or (Ph₃P)₂Ni(CO)₂]. The introduction of a halogen atom in the 9-position of the carboranyl nucleus has no substantial influence on the position of the CO band.

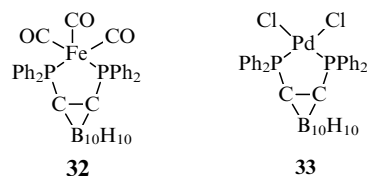
These complexes were found to be thermally unstable. On refluxing in high-boiling organic solvents, they lose CO and are thus converted into more stable complexes **30**.^{5,16}

Nickel dihalide complexes **31**, which are prepared by treatment of the corresponding nickeldicarbonyl complexes of halogenated *o*-carboranes with halogens, undergo a similar transformation.^{16,17}



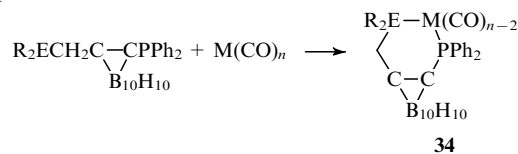
$n = 1-3$; $X = \text{Cl, Br}$; $Y = \text{Cl, Br, I}$.

Based on 1,2-bis(diphenylphosphino)-*o*-carborane **1**, irontricarbonyl **32** and palladium **33** complexes have also been obtained.¹⁸



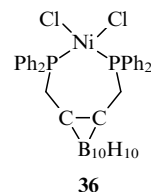
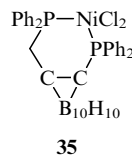
A large number of complexes with bidentate ligands containing two phosphorus atoms or a phosphorus and an arsenic atom have been synthesised.¹²

These ligands react with Ni(CO)₄ under mild conditions at 20 °C to give the corresponding complexes **34**; however, similar reactions with Mo, W, Cr and Fe carbonyls occur only on exposure to UV radiation.¹²

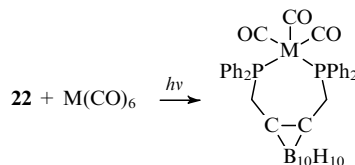


$R = \text{Me, Ph}$; $E = \text{P, As}$; $M = \text{Ni, Cr, Mo, W, Fe}$; $n = 4-6$.

The bis-phosphine ligands **18** and **22** readily react with NiCl₂ to yield complexes **35** and **36**, which are stable in air but rapidly decompose in alcoholic media.¹²

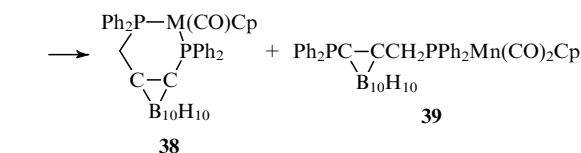
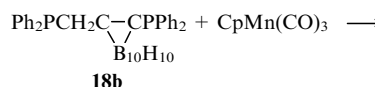
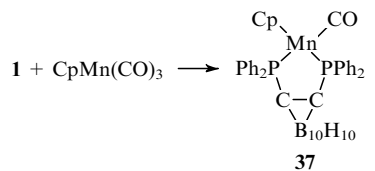


The reactions of the carboranylphosphine **22** with chromium, molybdenum and tungsten carbonyls occur only on exposure of benzene solutions of the reactants to UV radiation for 5–15 h.¹⁹



$M = \text{Cr, Mo, W}$.

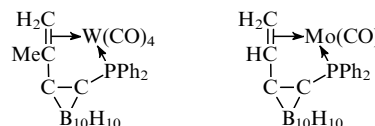
The carboranylphosphines **1** and **18b** react with cyclopentadienylmanganese tricarbonyl in different ways.¹⁹ In the case of **1**, the reaction yields complex **37**. In the latter case, complex **38** with a similar structure is formed together with compound **39** in which the carboranylphosphine **18b** acts as a monodentate ligand.¹⁹



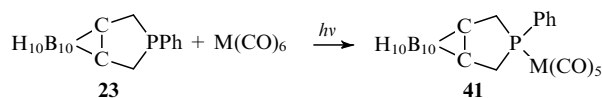
Cp = cyclopentadiene.

o-Carborane derivatives containing one diphenylphosphine group such as *o*-carboranyldiphenylphosphine **6a** ($R' = \text{Ph}$), 1-diphenylphosphinomethyl-2-dimethylarsino-*o*-carborane **18c**, 1-diphenylphosphino-2-methylthiomethyl-*o*-carborane **40** and 1-diphenylphosphino-2-isopropenyl-*o*-carborane **6e** ($R' = \text{Ph}$) react with CpMn(CO)₃ (Cp is cyclopentadiene) with replacement of only one CO group.¹⁹

Diphenylphosphinocarboranes **6d,e** ($R' = \text{Ph}$) containing a vinyl or isopropenyl substituent in the 2-position react with W(CO)₄ and (COD)₂Mo(CO)₄ (COD is cyclooctadiene) to give complexes in which the C=C double bond participates in coordination.¹²



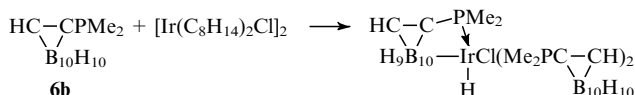
When THF solutions containing *o*-carboranylphospholane **23** ($R = \text{Ph}$) and Cr, Mo or W hexacarbonyl are irradiated by UV light, one CO group is displaced to give complexes **41**.⁶



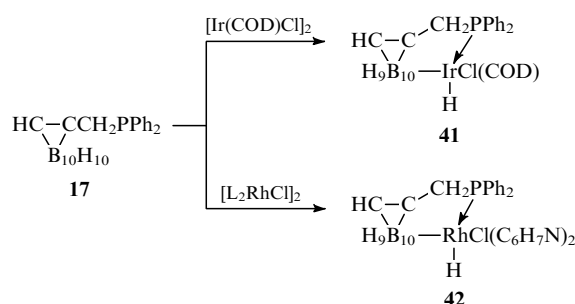
$M = \text{Cr, Mo, W}$.

All the complexes described above are solids stable in air; however, most of them decompose in the light. In the structures of these complexes, the metal is coordinated by the lone electron pair of the phosphorus atom.

Transition metal complexes with carboranylphosphines containing B–M bonds that involve the boron atom in the 3(6)-position of the carborane ring, in addition to the P–M bonds, have also been synthesised. A complex of this type is formed, for example, when the carboranylphosphine **6a** ($R' = \text{Me}$) is made to react with the iridium cyclooctene complex.²⁰



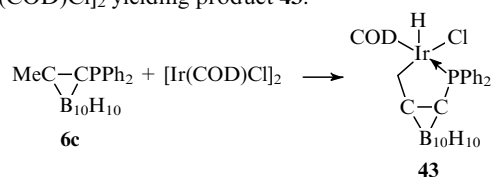
Other representatives of this type of complexes, for example **41** and **42**, have been prepared by the reactions of (*o*-carboranyl-methyl)diphenylphosphine **17** with iridium and rhodium complexes in the presence of 4-methylpyridine.²¹



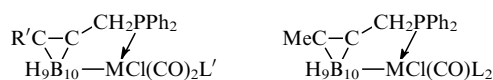
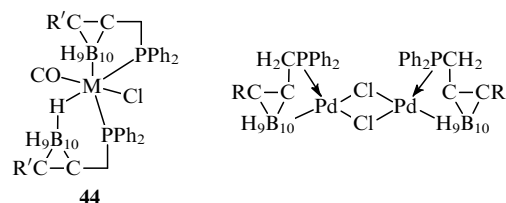
$\text{L} = \text{CO}, \text{C}_8\text{H}_{14}$.

The reaction of **17** with $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (in hydrocarbon solvents at 25 °C) yields a square-planar d^8 -complex of rhodium, *trans*-(*o*-HCB₁₀H₁₀CCH₂PPh₂)₂Rh(CO)Cl, which does not give intramolecular metallation products on heating with excess phosphine or 4-methylpyridine.²¹

Further studies of cyclometallation of carborane-containing phosphines with Rh(I) and Ir(I) complexes have shown that both the structure and the nature of the substituent in the 1-position of the carborane nucleus can have a substantial effect on the reaction pathway and on the nature of the final product.²² It was found that (2-methyl-*o*-carboranyl)diphenylphosphine **6b** ($R' = \text{Ph}$) does not react with Rh(I) complexes but does react with $[\text{Ir}(\text{COD})\text{Cl}]_2$ yielding product **43**.



In addition to *B*-metallated Rh and Ir complexes of carboranylphosphines, a series of Pd, Os and Ru complexes of this type have also been prepared by reductive carboranylation.^{23–25}



$\text{M} = \text{Ru}, \text{Os}; \text{R} = \text{H}, \text{Pr}^i; \text{R}' = \text{H}, \text{Me};$

$\text{L} = \text{N} \begin{array}{c} \diagup \text{C} \diagdown \\ \text{Me} \end{array}; \text{L}_2 = \begin{array}{c} \diagup \text{C} \diagdown \\ \text{N} \end{array}; \text{L}' = \text{R}'\text{C} \begin{array}{c} \diagup \text{C} \diagdown \\ \text{B}_{10}\text{H}_9 \end{array} \text{CH}_2\text{PPh}_2.$

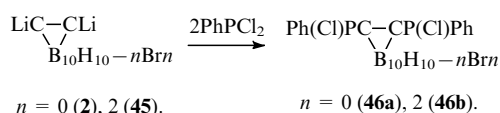
Apart from the *B*-metallated carboranylphosphine ligand, the complexes **44** ($\text{M} = \text{Ru}, \text{Os}$) also contain a carboranylphosphine coordinated to the metal atom through the phosphorus atom and the hydrogen atom in the 9-position of the carboranyl nucleus.²⁵

2. Carborane-containing derivatives of acids of trivalent phosphorus

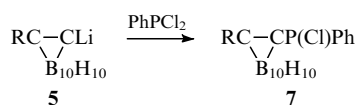
a. Carborane-containing halophosphines

The main method for the synthesis of carborane-containing halophosphines is based on the reaction of lithio-derivatives of carboranes with halophosphines or with PCl_3 .

The first carboranylchlorophosphines **46a,b** were prepared from 1,2-dilithio-*o*-carborane **2**³ or its *B*-bromo-substituted analogue **45**⁴ and PhPCl_2 .

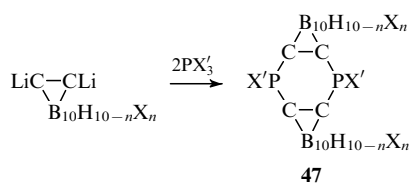


The carborane-containing chloro(phenyl)phosphines **7** were obtained in a similar way from the lithio-derivatives of 1-substituted *o*-carboranes **5** and PhPCl_2 .⁷



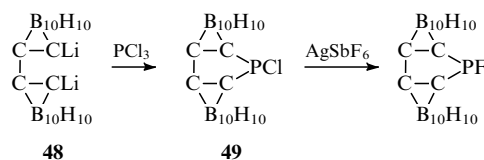
$\text{R} = \text{Me}, \text{Ph}.$

Dilithio-carboranes react with PCl_3 , PBr_3 and PI_3 to give dimeric halodicarboranodiphosphinanes **47**.^{3,4,26}

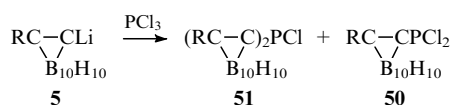


$n = 0-10; \text{X}, \text{X}' = \text{Cl}, \text{Br}, \text{I}.$

The interaction of the dilithio-derivative of bis-*o*-carborane **48** with PCl_3 affords cyclic chlorophospholane **49** in 94% yield. By treatment with AgSbF_6 , **49** has been converted into the corresponding fluorophospholane.²⁷

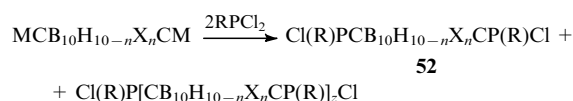


The reaction of PCl_3 with the lithio-derivatives **5** results in the formation of bis(*o*-carboranyl)chlorophosphines **51** together with *o*-carboranyldichlorophosphines **50** as an impurity.^{7,28}



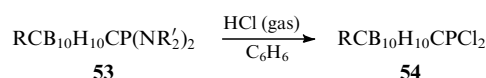
$\text{R} = \text{HC}=\text{CH}_2, \text{MeC}=\text{CH}_2, \text{Me}, \text{Ph}.$

1,7-Dimetallated *m*-carboranes react with PCl_3 , PhPCl_2 or AlkPCl_2 to give bis(dichlorophosphino)-, bis[(chloro)phenylphosphino]- or bis(alkylchlorophosphino)-*m*-carboranes **52** together with oligomeric products. No cyclic phosphines have been detected among the reaction products.^{29–31}



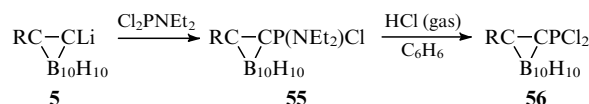
$n = 0–10$; $z = 2–10$; $M = \text{Li, Na, K}$; $R = \text{Cl, Ph, Alk}$;
 $X = \text{F, Cl, Br, I}$.

A drawback of the above methods is that some difficulties arise in the purification of the carboranylchlorophosphines. Treatment of carborane-containing phosphamidites **53** with dry HCl in benzene permits preparation of the corresponding carboranylchlorophosphines **54** in yields of up to 95% and in a highly pure state.^{32–34}



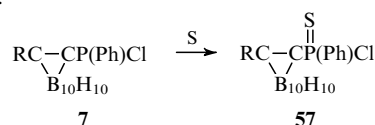
$R = o\text{-H, } m\text{-H, } o\text{-Me, } o\text{-Ph, } o\text{-MeC}=\text{CH}_2$; $R' = \text{Me, Et}$.

o-Carboranyl(dialkylamino)chlorophosphines **55**, which can be easily prepared by treatment of lithio-derivatives of the substituted carboranes **5** with (dialkylamino)dichlorophosphines, react with HCl in a similar way.³³



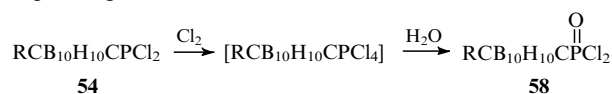
$R = \text{Me, Ph}$.

Carboranyl-containing chlorophosphines are much less reactive than alkyl- or arylchlorophosphines. This may be due both to the steric factors and to the electronic influence of the electron-deficient carboranyl group. They are stable with respect to atmospheric oxygen at room temperature. Carboranyldichlorophosphines and dicarboranylchlorophosphines do not add sulfur under drastic conditions even in the presence of AlCl_3 or FeCl_3 , whereas *o*-carboranyl(chloro)phenylphosphines **7** add sulfur upon heating to 170–180 °C and are thus converted into the corresponding (*o*-carboranyl)phenylphosphinothioic chlorides **57**.^{11, 32}



$R = \text{Me, Ph}$.

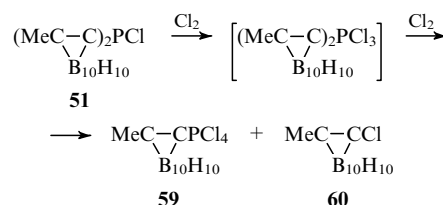
The addition of chlorine to carborane-containing chlorophosphines occurs readily and is usually accompanied by an exothermal effect. The addition products have not been isolated; however, it has been assumed that the reaction involves intermediate formation of carboranylchlorophosphoranes, which are readily hydrolysed in moist air or in aqueous dioxane to give the corresponding dichlorides **58**.



$R = o\text{-Me, } o\text{-Ph, } m\text{-H}$.

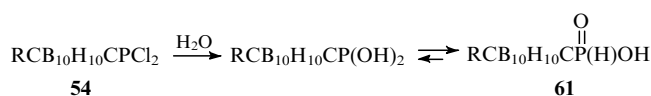
At the same time, it has been reported but not confirmed experimentally⁷ that the reaction of chlorobis(2-methyl-*o*-carboranyl)phosphine **51** with excess chlorine affords crystalline methyl-*o*-carboranyltetrachlorophosphorane **59** and 2-chloro-1-methyl-

o-carborane **60**, i.e. it is accompanied by cleavage of one phosphorus–carboranyl carbon bond.



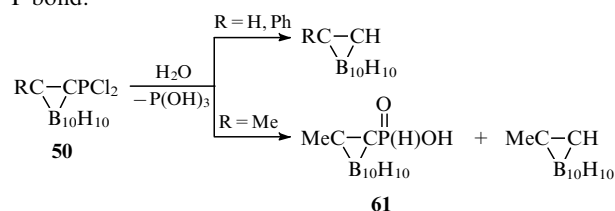
Chlorobis(2-phenyl-*o*-carboranyl)phosphine **51** ($R = \text{Ph}$) does not react with chlorine;⁷ this can be explained by steric hindrance caused by the presence of two 2-phenyl-*o*-carboranyl groups at the phosphorus atom.

Carborane-containing chlorophosphines readily react with various nucleophiles, for example, water, alcohols, amines, azides and others. However, these reactions are often accompanied by cleavage of the P–C bond, the reaction pathway depending both on the nature of the attacking nucleophile and on the structure of carboranylchlorophosphine. It was shown that *o*- and *m*-carboranyldichlorophosphines **54** are smoothly hydrolysed at room temperature by atmospheric moisture to give the corresponding carboranylphosphonous acids. According to IR spectral data, these compounds contain pentavalent phosphorus, despite the electron-withdrawing effect of the carboranyl groups.^{33, 34}

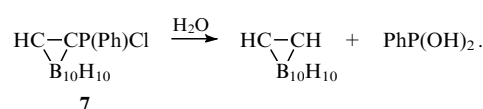


$R = m\text{-H, } o\text{-H, } o\text{-Me, } o\text{-Ph}$.

Hydrolysis of *o*-carboranyldichlorophosphines **50** ($R = \text{H, Ph}$) in aqueous dioxane in the presence of hydrochloric acid gives only the products of rupture of the P–C(carborane) bond, whereas dichloro(2-methyl-*o*-carboranyl)phosphine **50** ($R = \text{Me}$) is mostly converted under the same conditions into (2-methyl-*o*-carboranyl)phosphinic acid **61** ($R = \text{Me}$) (yield 75%) and also into the products of rupture of the C–P bond.³² Probably, this reaction pathway is due to the influence of the methyl substituent, which decreases the electron-withdrawing ability of the carboranyl group and increases the strength of the C–P bond.

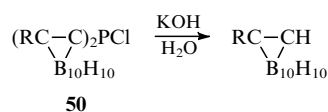


o-Carboranylchlorophenylphosphine is fairly unstable with respect to hydrolysis, apparently owing to the presence of three electron-withdrawing substituents at the phosphorus atom; it is cleaved into carborane and phenylphosphonous acid even by the atmospheric moisture.⁷



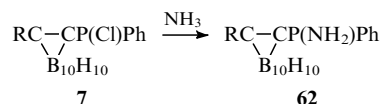
The easy rupture of the C–P bond in the carborane-containing chlorophosphines may be due to the fact that a carboranyl group attached to a phosphorus atom can act as a pseudo-halogen under certain conditions. Similar behaviour has been observed for carboranylphosphinous acids in which the phosphorus–C(carborane) bond is cleaved on heating of their aqueous solutions.³²

Bis(*o*-carboranyl)chlorophosphines are resistant to the action of water; their alkaline hydrolysis gives only products resulting from cleavage of the C–P bond.³²



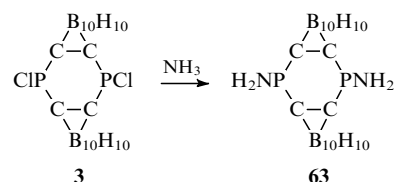
R = Me, Ph.

The reactions of carboranyl-containing chlorophosphines with ammonia, unlike their reactions with water, occur with replacement of the chlorine atom to give the corresponding amides **62**, the C–P bond remaining intact.⁷

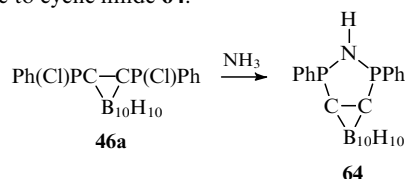


R = Me, Ph.

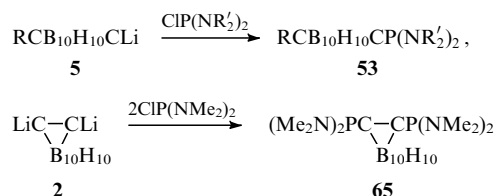
The dimeric dichlorophosphine **3** reacts with ammonia in a similar way yielding cyclic diamide **63**.³



The interaction of dry ammonia with 1,2-bis(chlorophenylphosphino)carborane **46a** involves both chlorine atoms and gives rise to cyclic imide **64**.

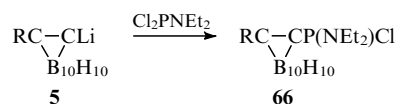


Dialkylamido-derivatives of carborane-containing acids of trivalent phosphorus have been described. These compounds were obtained as intermediates in the synthesis of carboranyl-chlorophosphines; the methods for their preparation were based on the reactions of monolithiocarboranes^{11, 32, 34} or dilithiocarborane³⁵ with chlorobis(dialkylamino)phosphines.



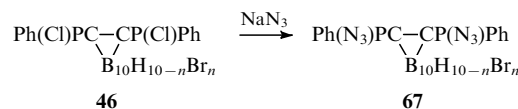
R = *m*-H, *o*-H, *o*-Me, *o*-Ph; R' = Me, Et.

The attempts to prepare bis(carboranyl)dialkylamino-phosphines by treating aminodichlorophosphines with the lithio-derivatives of *o*-carboranes **5** were unsuccessful. In this case, only one chlorine atom was substituted resulting in the formation of dialkylamino(*o*-carboranyl)chlorophosphines **66**. The second chlorine atom was not replaced, apparently, due to steric hindrance.^{11, 33}



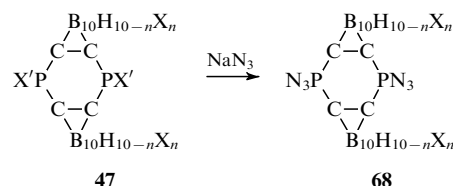
R = Me, Ph.

Carborane-containing chlorophosphines readily react with sodium azide. For example, bromo-substituted 1,2-bis(azidophenylphosphino)-*o*-carboranes **67** have been obtained in this way.^{3, 4, 26}



$n = 0-2$.

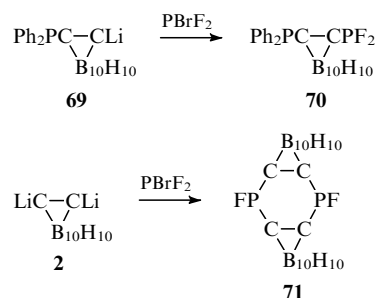
The bis-azide **67** is unstable and polymerises at 60 °C. Similarly, cyclic bis-halophosphines **47** have been converted into cyclic bis-phosphine azides **68**.^{3, 4, 26}



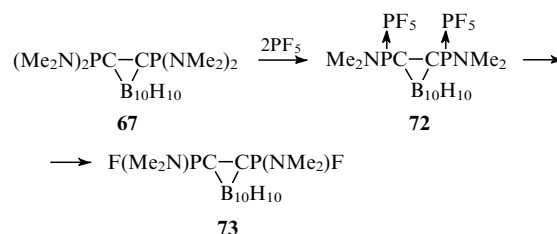
$n = 0-10$; X = Cl, Br; X' = Cl, Br, I.

These compounds readily react with tertiary phosphines to give the corresponding phosphazo-derivatives. Polymers based on these derivatives possess valuable properties.^{4, 26}

Carborane-containing fluorophosphines and their platinum complexes were synthesised for the first time in the late 70s and early 80s. Various methods have been used for this purpose. Thus treatment of 2-lithio-1-diphenylphosphino-*o*-carborane **69** with PBrF₂ yielded 2-difluorophosphino-1-diphenylphosphino-*o*-carborane **70**.³⁶ A similar reaction involving dilithio-*o*-carborane **2** resulted in the formation of cyclic difluorophosphine **71**.³⁵



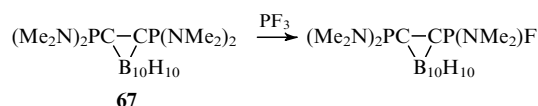
Fluoroamides were synthesised by the reaction of PF₅ with 1,2-bis[bis(dimethylamino)phosphino]-*o*-carborane **67** ($n = 0$).³⁵ It was found that this reaction yields initially adduct **72** containing two PF₅ molecules; upon prolonged heating, it is converted into the corresponding fluorophosphine **73**, only one fluorine atom being introduced to each phosphorus atom.



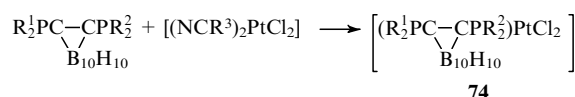
The adduct **72** is a complex containing a P(III)–P(V) bond. It has been assumed³⁸ that in acetonitrile solutions, this compound is ionic. This reaction has also been studied in relation to other compounds.³⁵⁻³⁸

Attempts to replace the NMe₂ group in the carborane-containing aminophosphine **67** by a fluorine atom by treating this compound with PF₃ were undertaken.^{35, 36} This reaction

occurred slowly: only one fluorine atom was introduced into the molecule upon heating the reaction mixture for several days.³⁶



Carborane-containing fluorophosphines are stable in air but are slowly hydrolysed in solution. On treatment with Pt(II) cyanide complexes, they are readily converted into the corresponding *cis*-complexes **74**, their yields ranging from 42% to 85%.³⁹

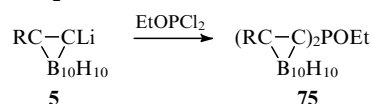


R¹ = Ph, NMe₂; R² = F, C₆F₆, Ph, NMe₂; R³ = Me, Ph.

b. Carborane-containing esters of trivalent phosphorus acids

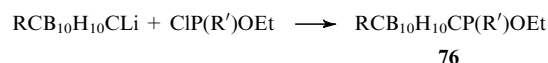
Carborane-containing esters of acids containing trivalent phosphorus have been studied in detail. Esters in which the phosphorus atom is either directly linked to the carborane carbon atom or separated from it by other atoms as well as sulfur- and selenium-containing esters in which the phosphorus atom is connected to the boron atom of the carboranyl group *via* sulfur or selenium have been synthesised.

Carborane-containing esters of trivalent phosphorus acids in which the phosphorus atom is directly attached to the carbon atom of the carborane nucleus have been prepared by several methods. The most reliable procedure is based on the reaction of lithiocarboranes with the corresponding phospho- or phosphonochloridites. For example, ethyl bis(*o*-carboranyl)phosphinites **75** have been prepared in yields of up to 70% by the reaction of the corresponding 2-substituted 1-lithio-*o*-carboranes **5** with EtOPCl₂.⁴⁰



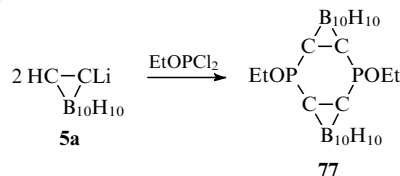
R = Me, Ph, MeC=CH₂.

Esters of carborane-containing phosphinous and phosphonic acids **76** have been synthesised in a similar way.^{41–43}

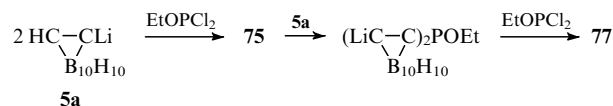


R = *o*-H, *m*-H, *p*-H, *o*-Me, *o*-Ph, *o*-MeC=CH₂; R' = Me, OEt.

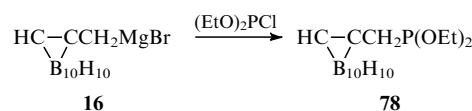
The lithio-derivative of the unsubstituted carborane reacts with ethyl phosphodichloridite to give only cyclic diphosphinite **77**.⁴⁰



This may be due to the fact that 1-lithio-*o*-carborane **5a** disproportionates^{44,45} to give 1,2-dilithio-*o*-carborane **2** and carborane, and the dilithio-derivative **2** reacts with ethyl phosphodichloridite. However, it cannot be ruled out that the compound **77** results from metallation of the intermediate bis(*o*-carboranyl)phosphinite **75** by 1-lithio-*o*-carborane **5a** and subsequent interaction of the lithio-derivative with ethyl phosphodichloridite.

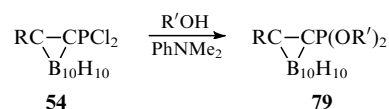


Diethyl (*o*-carboranylmethyl)phosphonite **78** has been synthesised by the reaction of diethyl phosphodichloridite with (1-bromomagnesiomethyl)carborane **16**.⁴⁶



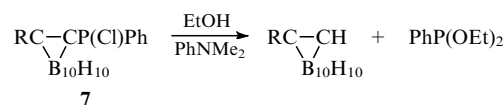
Esters of carborane-containing acids of trivalent phosphorus can be obtained by the interaction of alcohols with the corresponding carboranylchlorophosphines. However, this method is inconvenient, because it is difficult to purify the reaction products. It has been reported³¹ that the treatment of 1,7-bis(dichlorophosphino)- or 1,7-bis(chlorophenylphosphino)-*m*-carboranes **52** with methanol gives rise to the corresponding tetramethyl or dimethyl esters of carborane-containing acids of trivalent phosphorus. However, no evidence confirming the structures of the reaction products was presented in the study cited.

Reactions of carborane-containing chlorophosphines with alcohols in the presence of dimethylaniline or sodium ethoxide have been studied. The reaction pathway was found to depend both on the structure of the corresponding chlorophosphine and on the reaction conditions. When 2-substituted *o*-carboranyldichlorophosphines **54** are made to react with methanol or ethanol in the presence of dimethylaniline, the corresponding dialkyl phosphonites **79** are formed in yields of up to 80%.⁷



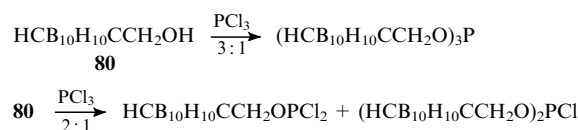
R = H, Me; R' = Me, Et.

The attempt to carry out the reaction between *o*-carboranyldichlorophosphines **16** and sodium ethoxide has led only to products resulting from the cleavage of the C–P bond.⁷ The reaction involving 2-substituted *o*-carboranylphenylchlorophosphines **6** occurs in a similar way. These substrates are cleaved even by alcohols under mild conditions in the presence of dimethylaniline. This was explained⁷ by the fact that phosphorus carries a phenyl group and a chlorine atom, in addition to the carboranyl group, and this decreases the strength of the C–P bond.⁷



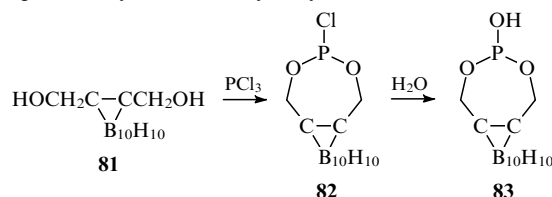
R = Me, Ph.

To synthesise carborane-containing esters of trivalent phosphorus acids and thioacids, carborane-containing alcohols and dithiols have also been used. For example, the reaction of 1-hydroxymethyl-*m*-carborane **80** with PCl₃ leads to the products of replacement of one, two or three chlorine atoms, depending on the ratio of the reactants.⁴⁷ Despite the absence of bases, no hydrogen phosphite was formed in the reaction.

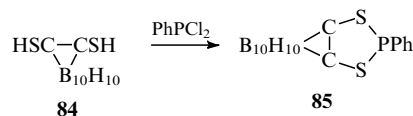


1,2-Bis(hydroxymethyl)-*o*-carborane **81** has also been introduced in the reaction with PCl₃. This gave the corresponding

cyclic phosphochloridite **82**, which was converted into hydrogen phosphite **83** by controlled hydrolysis.⁴⁸



Cyclic carborane-containing phenylphosphonodithioite **85** has been prepared by the reaction of carborane-1,2-dithiol **84** with PhPCl_2 .⁴⁹

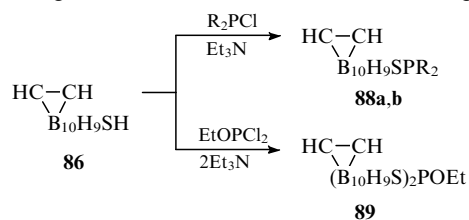


The reactivity of carboranyl or carboranylmethyl esters of trivalent phosphorus acids is markedly lower than that of similar esters containing no carboranyl groups. It depends both on the number of carboranyl groups attached to the phosphorus atom and on the character of the substituents in the carborane nucleus.

Carboranyl phosphonites are stable with respect to atmospheric oxygen and are not oxidised even upon heating to 100 °C; however, they are readily oxidised by N_2O_4 .⁵⁰ The addition of sulfur, CuCl and azides to these derivatives as well as the Arbuzov and Perkow reactions occur less readily than those for phosphonites devoid of the carboranyl group.^{41–43}

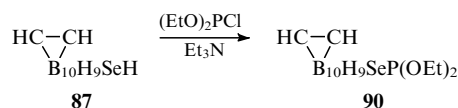
Bis(carboranyl)phosphinites do not add sulfur, do not form complexes with CuCl , do not react with azides and do not enter into the Arbuzov reaction.⁴⁰ The inertness of these compounds can be due both to the steric hindrance caused by the two carboranyl groups and to the large overall electron-withdrawing effect of these groups.⁴⁰

B-substituted carborane-containing esters of trivalent phosphorus thioacids^{51–53} and selenoacids⁵⁴ have been synthesised from *o*-carborane-9-thiol **86** or *o*-carborane-9-selenol **87**. The reactions were carried out in the presence of triethylamine under an inert atmosphere at –30 °C. When the compound **86** was made to react with EtOPCl_2 , $(\text{EtO})_2\text{PCl}$ and Ph_2PCl , the corresponding thioesters **88** and **89** were obtained in high yields.^{51–53}

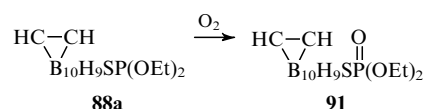


R = EtO (**a**), Ph (**b**).

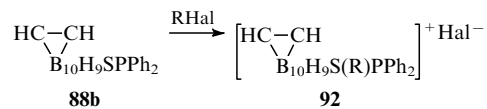
When $(\text{EtO})_2\text{PCl}$ reacts with *o*-carborane-9-selenol **87**, the corresponding selenoester **90** is formed but the researchers have not been able to isolate it in a pure state.⁵⁴



o-Carboran-9-yl esters of trivalent phosphorus thioacids of type **88a,b** add sulfur and selenium; they form complexes with metal carbonyls and enter into the Arbuzov and Perkow reactions. As a rule, these thioesters are quite stable in air; however, the phosphorothioite **88a** is oxidised by atmospheric oxygen to phosphothioate **91** even during chromatography on silica gel.⁵²

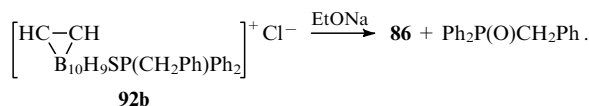


On treatment with alkylating reagents, phosphinothioite **88b** is converted into stable quasi-phosphonium salts **92**.⁵⁵

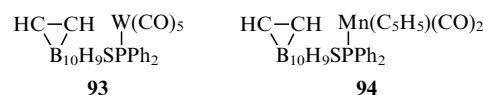


92	R	Hal	Yield (%)
a	Me	I	98
b	PhCH_2	Cl	50
c	$\text{H}_2\text{C}=\text{CHCH}_2$	Br	62

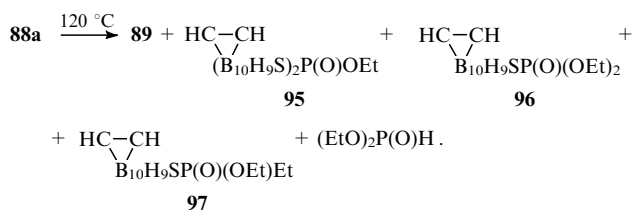
It was shown that treatment of the salt **92b** with sodium ethoxide in ethanol results in the rupture of the P–S bond and gives the thiol **86** in an almost quantitative yield, together with benzyldiphenylphosphine oxide.⁵⁵



The phosphinothioite **88b** forms complexes **93** and **94** with pentacarbonyl tetrahydrofuranotungsten and with dicarbonyl cyclopentadienyltetrahydrofuranomanganese, respectively.⁵³



The phosphinothioite **88b** is fairly stable when heated to 200 °C under an argon atmosphere, whereas the phosphorothioite **88a** decomposes even at 120 °C to give a mixture of products containing the compound **89** (29.9%), *O*-ethyl *S,S*-bis(*o*-carboran-9-yl) phosphodithioate **95** (4.8%), *O,O*-diethyl *S*-*o*-carboran-9-yl phosphothioate **96** (10.6%), *O*-ethyl *S*-*o*-carboran-9-yl ethylphosphonothioate **97** (17.6%), $(\text{EtO})_2\text{PHO}$ (30.5%) and non-identified products (6%).⁵⁵



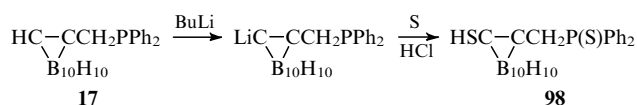
III. Carborane-containing derivatives of pentavalent phosphorus

Derivatives of pentavalent phosphorus constitute a large portion of all known phosphorus-containing carboranes. These compounds are synthesised by reactions typical of derivatives of both trivalent and pentavalent phosphorus.

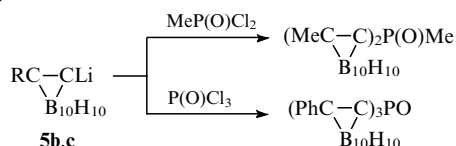
1. Carboranylphosphine oxides and sulfides, derivatives of carborane-containing phosphinic and phosphonic acids

Syntheses of some carborane-containing phosphine oxides and sulfides have been mentioned in Section II.1.b. These derivatives were synthesised by addition of oxygen or sulfur to the corresponding carborane-containing phosphines. 2-Diphenylphosphinothiomethyl-*o*-carboranethiol **98** has been prepared using a

different approach consisting in metallation of *o*-carboranylmethylidiphenylphosphine **17** and treatment of the resulting lithio-derivative with sulfur. The reaction product was isolated after acidification by hydrochloric acid.¹²

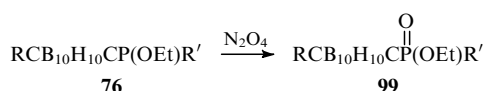


Bis- and tris-carboranylphosphine oxides have been synthesised by treatment of the lithio-derivatives of 2-substituted carboranes **5b,c** with methylphosphonoyl dichloride or with phosphorus oxychloride.³³



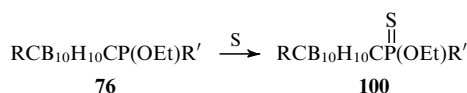
R = Me (**b**), Ph (**c**).

As noted above, carborane-containing esters of acids of trivalent phosphorus are stable against oxidation with atmospheric oxygen; however, they are readily oxidised by N₂O₄ to give the corresponding esters containing pentavalent phosphorus in high yields.⁵⁰ For example, this procedure was used to synthesise compounds **99**.



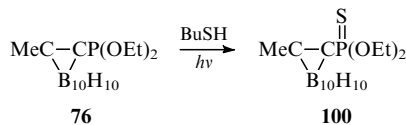
R = *p*-H, *m*-H, *o*-Me, *o*-Ph, *o*-MeC=CH₂; R' = Me, OEt.

Carborane-containing phosphonothioates and phosphinothioates **100** can be prepared by addition of sulfur, which occurs only on heating to 100–120 °C. The relatively low reactivity of the compounds studied with respect to sulfur is apparently due to the electron-withdrawing effect of the carboranyl group.⁴²

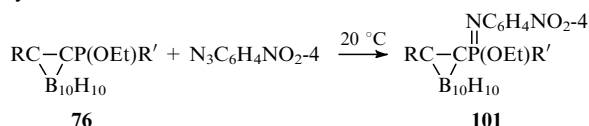


R = *o*-H, *m*-H, *o*-Me, *o*-MeC=CH₂; R' = Me, OEt.

O,O-Diethyl (2-methyl-*o*-carboranyl)phosphonothioate **100** (R = Me, R' = OEt) was also obtained by the reaction of the corresponding carboranylphosphonite **76** with butanethiol under UV radiation.⁴²



On treatment with 4-nitrophenyl azide, carborane-containing esters of acids of trivalent phosphorus **76** are converted relatively easily into imino-derivatives **101**.^{42, 43}



R = H, Me, Ph, MeC=CH₂; R' = Me, OEt.

However, this reaction occurs more slowly than that involving similar esters of acids of trivalent phosphorus devoid of the carboranyl group. It was also found that substituents at the phosphorus atom as well as those in the *o*-carborane nucleus have a substantial influence on the reactivity.⁴³

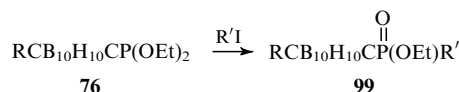
Based on the dissociation constants of imidophosphinates **101**, the σ^{P} constants for substituted *o*-carboranyl groups were calculated (Table 1).⁴³ The results obtained confirm the electron-withdrawing properties of the carboranyl group.

Table 1. Dissociation constants and σ^{P} values for imidophosphinates **101** (R' = Me).⁴³

R	pK _a	σ^{P}
H	5.48	2.10
Me	6.10	1.79
MeC=CH ₂	5.83	1.92
Ph	5.68	2.00

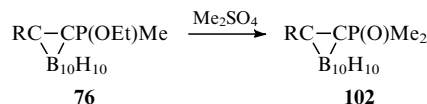
The Arbuzov reaction can also be used to prepare carborane-containing derivatives of pentavalent phosphorus; however, it also occurs under more drastic conditions than the same reaction for esters of trivalent phosphorus acids devoid of the carboranyl group.

The reaction of diethyl carboranylphosphonite with MeI in acetonitrile carried out by heating the reactants in a tube (100–140 °C) affords the corresponding derivatives of pentavalent phosphorus **99**, their yields ranging from 50% to 73% depending on the character of the substituent at the phosphorus atom. The reaction occurs most readily for the carborane-containing methyl phosphinites **76** (R' = Me).^{42, 43, 50} Ethyl iodide reacts in a similar way.⁴²



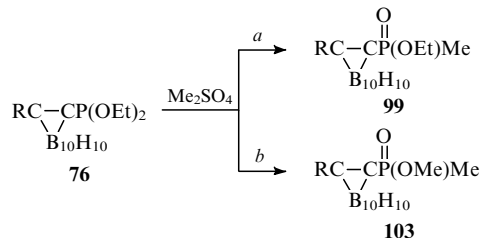
R = *m*-H, *p*-H, *o*-Me, *o*-Ph; R' = Me, Et.

The reaction with dimethyl sulfate occurs under substantially milder conditions (at 20 °C) giving rise to compounds **102** in yields of up to 81%.⁴³



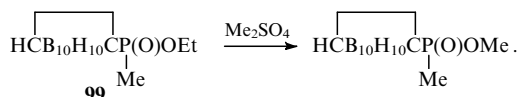
R = H, Me.

To carry out a similar reaction with diethyl (*o*-carboranyl)-phosphonites, heating to 110–120 °C is required. Whereas the transformation of diethyl (2-methyl-*o*-carboranyl)phosphonite **76** (R = Me) gave ethyl (2-methyl-*o*-carboranyl)methyl-phosphinate **99** in 78% yield, in the case of *o*-carboranylphosphonites **76** (R = H, MeC=CH₂), the reaction is accompanied by transesterification giving the corresponding methyl (*o*-carboranyl)methyl-phosphinates **103** in yields of up to 56%.⁵⁶

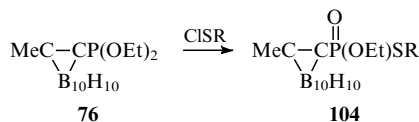


(a) R = Me; (b) R = H, MeC=CH₂.

Transesterification also occurs when ethyl (*p*-carboranyl)-methylphosphinate is heated with excess Me₂SO₄.⁵⁶

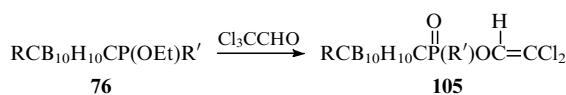


When diethyl *o*-carboranylphosphonites are treated with sulfonyl chlorides, the Arbuzov reaction smoothly occurs.^{41, 42} For example, the reactions with butylsulfonyl chloride and 2,4-dinitrophenylsulfonyl chloride in tetrachloromethane gave the corresponding thioesters **104** in yields of up to 90%.



R = Bu, 2,4-(NO₂)₂C₆H₃.

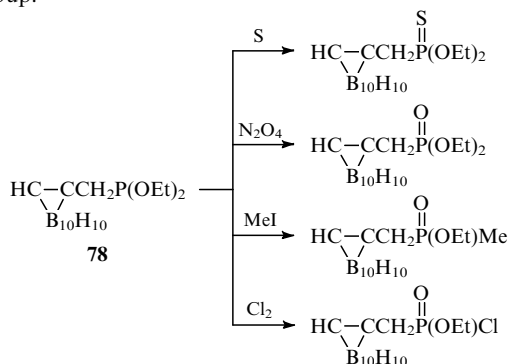
Several examples of the Perkow reaction have been reported. When the compounds **76** have been made to react with a large excess of chloral without a solvent, the corresponding dichlorovinyl carboranylphosphonates and carboranylphosphinates **105** have been obtained in 44% to 90% yields.^{43, 50}



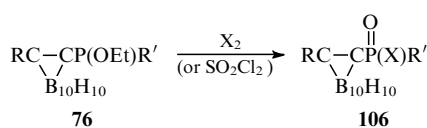
R = *p*-H, *m*-H, *o*-H, *o*-Me, *o*-Ph, *o*-MeC=CH₂; R' = Me, OEt.

(Carboranyl)methylphosphinites enter into this reaction much more readily than carboranylphosphonites. In addition, the ease of this reaction depends on the electron-withdrawing properties of the carboranyl groups, which are determined in this particular case by the nature of the carboranyl nucleus. The substituents present in these nuclei make only a minor contribution to the overall electronic effect of the carboranyl groups but cause substantial steric effects.^{43, 50}

Carborane-containing esters of acids of pentavalent phosphorus in which the carboranyl group is separated from the phosphorus atom by a methylene bridge are also known. These compounds have been prepared by means of standard reactions typical of esters of trivalent phosphorus acids devoid of the carborane group.⁴⁶

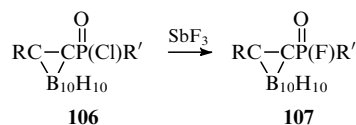


Chlorides and bromides of *o*-carborane-containing acids of pentavalent phosphorus **106** have been synthesised by treating the esters derived from carborane-containing acids of trivalent phosphorus **76** with sulfuryl chloride, chlorine or bromine.^{40, 42, 50}



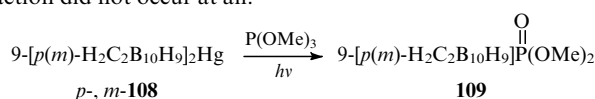
R = Ph, MeC=CH₂; R' = Me, OEt, —C—CH— $\text{B}_{10}\text{H}_{10}$; X = Cl, Br.

Fluorides **107** were prepared by treatment of the corresponding chlorides **106** with antimony trifluoride.⁵⁰



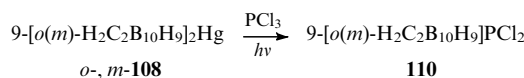
R = Ph, MeC=CH₂; R' = Me, OEt.

The first representatives of carborane-containing acids of pentavalent phosphorus in which the phosphorus atom is linked directly to the boron atom in the 9-position of the carboranyl group were obtained by the reaction of bis(*p*- or *m*-carboran-9-yl)mercury **108** with trimethyl phosphite under UV irradiation. Dimethyl (*p*-carboran-9-yl)phosphonate **109** was synthesised in this way in 60% yield. However, dimethyl (*m*-carboran-9-yl)phosphonate *m*-**109** was obtained by this procedure only in 5% yield, and in the case of bis(*o*-carboran-9-yl)mercury, the reaction did not occur at all.⁵⁷

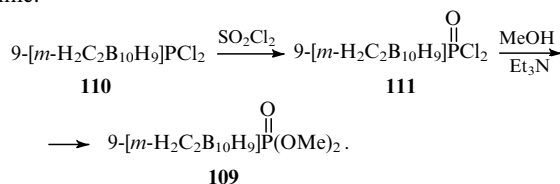


The σ^Φ constants for 9-*p*- and 9-*m*-carboranyl groups were found to be equal to −1.68 and −1.81, respectively, which points to electron-donating properties of these groups.⁵⁷

Bis(*o*-carboran-9-yl)mercury **108** reacts with PCl₃ on exposure to UV radiation to give the corresponding dichlorophosphine **110** in 5% yield. The *m*-carboranylmercury derivative reacts in a similar way (yield 10%).

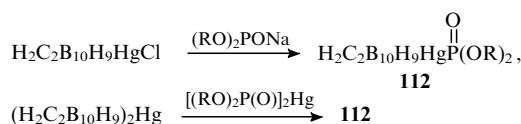


m-Carboran-9-yl dichlorophosphine **110** has been oxidised by SO₂Cl₂ to the corresponding phosphonyl dichloride **111**; the latter was converted into dimethyl (*m*-carboran-9-yl)phosphonate **109** by the reaction with methanol in the presence of triethylamine.^{58, 59}



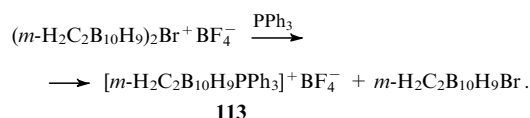
The results of X-ray diffraction and IR spectroscopy studies of dimethyl (*p*- and *m*-carboran-9-yl)phosphonates **109** have shown that their crystals contain hydrogen bonds; *p*-carborane-derivatives were found to form dimers.^{57, 60}

Carborane-containing derivatives of acids of pentavalent phosphorus **112** in which the 9-position of an *o*-, *m*- or *p*-carboranyl group is linked to the phosphorus atom via a mercury atom have been synthesised.^{61, 62}



R = Me, Et, Prⁱ.

Synthesis of (*m*-carboran-9-yl)triphenylphosphonium tetrafluoroborate **113** has been reported.⁶³ The researchers did not succeed in preparing a similar salt derived from *o*-carborane.

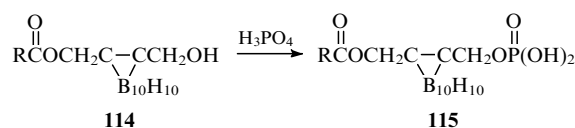


2. Derivatives of acids of pentavalent phosphorus containing a carboranyl group in the ester moiety of the molecule

Numerous examples of phosphorus acid esters containing a carboranyl group in the ester moiety of the molecule have been described. In these molecules, the carbon or boron atoms of the carboranyl moiety are linked to the phosphorus atom *via* sulfur or selenium atoms or *via* hydroxyalkyl or thioalkyl groups.

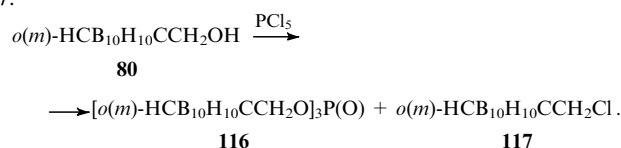
Carboranylalkyl esters of phosphorus-containing acids have been synthesised starting from various hydroxyalkylcarboranes.

The first *o*-carboranyl phosphates **115** were prepared by the reaction of monoacylated 1,2-bis(hydroxymethyl)-*o*-carboranes **114** with H_3PO_4 at 100–120 °C.⁶⁴

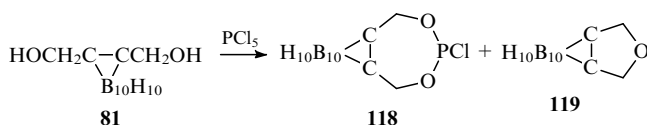


R = Alk.

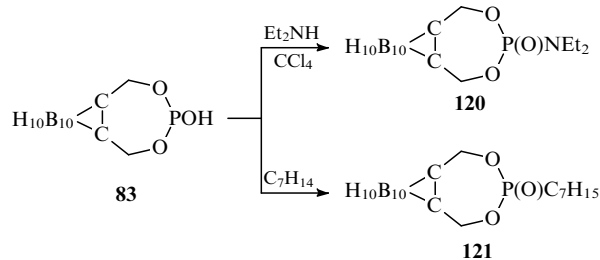
When hydroxymethyl-*o*-carboranes or -*m*-carboranes **80** are treated with PCl_5 , tris(carboranylmethyl) phosphates **116** are formed. The yield of the *m*-carborane derivative is 90%, whereas that of the *o*-carborane derivative does not exceed 26%. This reaction also yields the corresponding chloromethyl derivative **117**.^{65, 66}



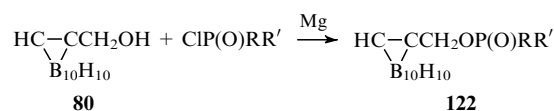
The reaction of PCl_5 with the diol **81** gives rise to a mixture of cyclic phosphochloridite **118** and 3,4-(1,2-*o*-carborano)oxolane **119** (yields 22% and 24%, respectively).⁶⁶



The diol **81** can also be used to synthesise cyclic esters of carborane-containing acids of pentavalent phosphorus. For example, the Todd–Atherton reaction involving the phosphite **83** has given carborane-containing amidophosphate **120**. Cyclic heptylphosphonate **121** was synthesised by the addition of the same phosphite to hept-1-ene.⁴⁸

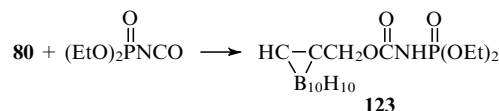


o-Carboranylmethyl phosphates **122** have been described. These compounds are formed in the reaction of hydroxymethyl-*o*-carborane **80** with POCl_3 or with monochlorophosphates in the presence of Mg as a catalyst.⁶⁷

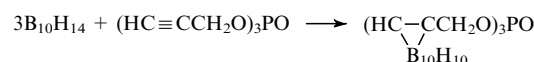
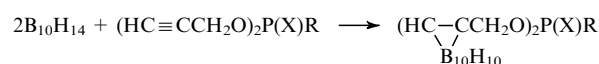
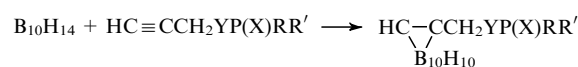


R, R' = Cl, OPh, OCH_2CF_3 .

The reaction of hydroxymethyl-*o*-carborane **80** with diethoxyphosphoryl isocyanate affords carbamate **123**.⁶⁸

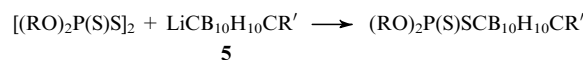


A series of *o*-carboranylmethyl esters of acids of pentavalent phosphorus have been synthesised by treatment of propynyl esters of the corresponding acids and thioacids with decaborane in the presence of dimethylaniline.^{69, 70} The yields of the products vary from 50% to 77%.



X, Y = O, S; R, R' = Me, OEt, Ph.

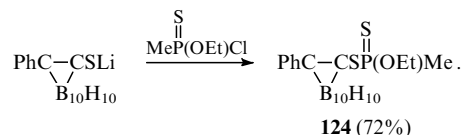
Several methods have been developed for the preparation of *S*-carboranyl esters of dithioacids of pentavalent phosphorus in which the sulfur atom is directly linked to the carbon atom of the carboranyl ring. According to one of these methods, lithiocarboranes **5** are made to react with bis(dialkoxythiophosphoryl) disulfides in benzene or in an ether–benzene mixture.⁷¹



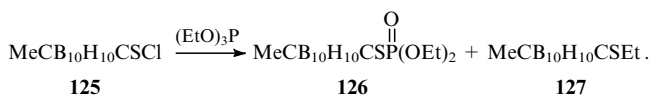
R = Me, Et, Prⁱ; R' = *o*-H, *m*-H, *o*-Me, *o*-Ph, ,

Unexpectedly, the reaction of equimolar amounts of bis(dialkoxythiophosphoryl) disulfides with lithio-*m*-carborane in an ether–benzene solvent mixture resulted in the formation of 1,7-bis(thiophosphorylthio)-*m*-carboranes. Similar transformations in benzene yielded only monosubstituted *m*-carboranyl phosphodithioates.

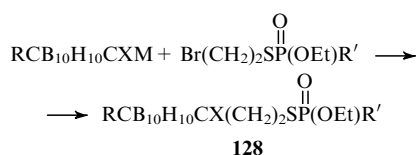
O-Ethyl *S*-(2-phenyl-*o*-carboranyl) methylphosphonodithioate **124** has been prepared by the reaction of lithium 2-phenyl-*o*-carboranethiolate with *O*-ethyl chlorophosphonothioate.⁷¹



To synthesise esters of thiophosphoric acid containing a 1-methyl-*m*-carboran-7-yl group, 1-methyl-*m*-carboran-7-ylsulfenyl chloride **125** has been introduced into the reaction with triethyl phosphite; this has given *O,O*-diethyl *S*-(1-methyl-*m*-carboran-7-yl) phosphothioate **126**. 7-Ethylthio-1-methyl-*m*-carborane **127** was isolated as a side product.⁷²

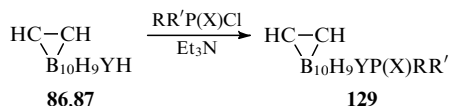


A series of *S*- β -carboranylthio(seleno)ethyl esters of thioacids of pentavalent phosphorus **128** have been synthesised by the reaction of *O*-ethyl *S*- β -bromoethyl methylphosphonothioates or *O,O*-diethyl *S*- β -bromoethyl phosphothioates with lithium or ammonium derivatives of carboranethiols or carboraneselenols.^{54, 71, 73}



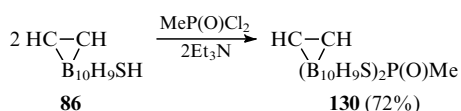
R = *m*-H, *o*-H, *o*-Me, *o*-Ph; R' = Me, OEt; X = S, Se; M = Li, Et₃NH.

Among carborane-containing acids of pentavalent phosphorus, some *B*-substituted thio- and selenoesters have also been synthesised and studied. Compounds of this type have been prepared from *o*-carborane-9-thiol **86** or selenol **87** using ordinary reactions typical of derivatives of phosphorus-containing acids. For example, treatment of the thiol **86** or the selenol **87** with pentavalent phosphorus acid chlorides in the presence of Et₃N has resulted in the synthesis of thio- or selenoesters containing one (**129**) or two (**130**) carboranyl groups.^{54, 73}



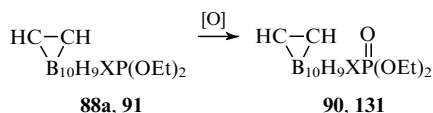
Y = S (**86**), Se (**87**).

R	R'	X	Y	Yield of 129 (%)
Me	OEt	O	S	69
Me	OC ₆ H ₄ NO ₂ -4	O	S	74
Ph	Ph	S	S	67
Me	OEt	O	Se	40
Me	OEt	S	Se	71



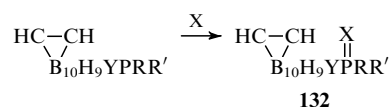
Other procedures for the synthesis of *B*-substituted derivatives of carborane-containing acids of pentavalent phosphorus are based on reactions of *o*-carboran-9-yl phosphorothioites or phosphoselenoites (see Section II).

O,O-Diethyl *S*-(*o*-carboran-9-yl) phosphinothioite **88a** is readily oxidised even during chromatography on silica gel to give phosphothioate **91** in 70% yield.⁵² The attempt to oxidise the corresponding selenium derivative with atmospheric oxygen gave only decomposition products; however, when furfural has been used as the oxidising agent, the corresponding phosphoselenoate **131** has been obtained in 50% yield.⁵⁴



X = S (**88a, 91**), Se (**90, 131**).

B-Substituted *o*-carborane-containing esters of thio- and seleno-acids of pentavalent phosphorus **132** can also be obtained in 60%–80% yields by the addition of sulfur or selenium to the corresponding thio- or seleno-derivatives of acids of trivalent phosphorus like **88** and **90**.^{51–54}



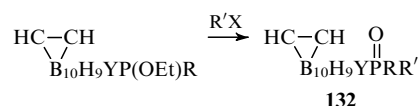
Y = S (**88**), Se (**90**).

R	R'	X	Y	Yield of 132 (%)
Ph	Ph	S	S	60
Ph	Ph	Se	S	79
OEt	OEt	O	S	70
OEt	OEt	S	S	82
OEt	OEt	Se	S	62
OEt	OEt	S	Se	76
OBu	OBu	S	Se	70
OEt	OEt	Se	Se	69
OBu	OBu	Se	Se	68
OEt	9- <i>o</i> -H ₂ C ₂ B ₁₀ H ₉ S	S	Se	93

The reaction conditions depend on the character of substituents at the phosphorus atom. When there are two ethoxy-groups, the addition of sulfur and selenium occurs at room temperature over a period of 36–40 h. Compounds in which two phenyl groups or two *o*-carboranyl groups are attached to the phosphorus atom react only on heating in benzene. In the case of *O*-ethyl *S,S*-bis(*o*-carboran-9-yl) phosphorodithioite **89**, the addition of selenium yields a product mixture that is difficult to separate.^{51, 55}

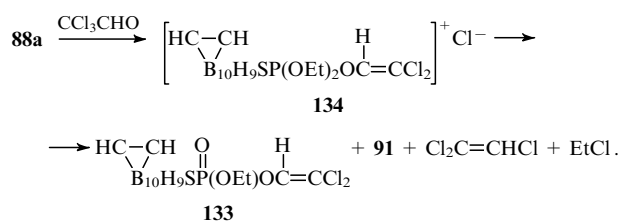
Several *B*-substituted esters of thioacids of pentavalent phosphorus **132** have been prepared by the Arbuzov reaction from the corresponding *S*-(*o*-carboran-9-yl) phosphorothioites and MeI or EtI.^{51, 52} The reactions involve only the phosphorus atom. No products resulting from the reaction at the sulfur atom were detected. When *Se*-(*o*-carboran-9-yl) phosphoselenoite was made to react with MeI, no Arbuzov products were isolated.⁵⁴ The reaction gave only non-identified phosphorus-containing compounds and bis(*o*-carboran-9-yl) diselenide. When Me₂SO₄ was used as the alkylating agent in the reaction with *O,O*-diethyl *Se*-(*o*-carboran-9-yl) phosphoselenoite **90**, the Arbuzov reaction product was isolated in 45% yield (see Scheme 1).⁵⁴

Scheme 1

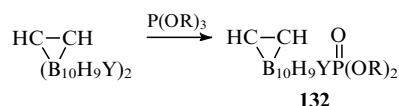


R	R'	Y	X	Yield of 132 (%)
OEt	Me	S	I	62
OEt	Et	S	I	65
OEt	Me	Se	SO ₄ Me	40
9- <i>o</i> -H ₂ C ₂ B ₁₀ H ₉ S	Me	S	I	75

Attempts were made to introduce *S*- and *O*-carboran-9-yl esters of acids of trivalent phosphorus into the Perkow reaction.^{51–53, 55} It was found that *O*-ethyl *S,S*-bis(*o*-carboran-9-yl) phosphorodithioite **89** and *S*-(carboran-9-yl) diphenylphosphinothioite **88b** do not react with chloral, whereas *O,O*-diethyl *S*-(*o*-carboran-9-yl) phosphorodithioite reacts with chloral according to Perkow to give *O*-ethyl *O*-(2,2-dichloroethenyl) *S*-(*o*-carboran-9-yl) phosphothioate **133** in a yield of 65%.^{52, 55} *O,O*-Diethyl *S*-(*o*-carboran-9-yl) phosphothioate **91** was also isolated from the reaction mixture. According to GLC analysis, the mixture also contained trichloroethylene and EtCl. This permitted the researchers to suggest that the process involves intermediate formation of quasi-phosphonium compound **134**.^{52, 55}

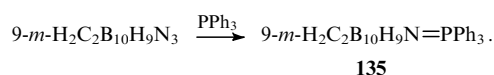


The reaction of bis(*o*-carboran-9-yl) diselenide or bis(*m*-carboran-9-yl) disulfide with trimethyl or triethyl phosphite is a convenient method for the preparation of *B*-substituted carboranyl esters of phosphothioic and phosphoselenic acids like **132**.^{74, 75}

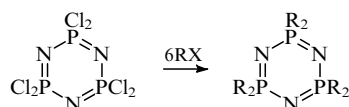


R	Y	Yield of 132 (%)
Me	Se	68
Et	Se	72
Et	S	71

In the series of *B*-substituted phosphorus-containing carboranes, synthesis of carborane-containing phosphinimine **135** is noteworthy. This synthesis has been accomplished by the reaction of *m*-carboran-9-yl azide with PPh_3 .⁷⁶

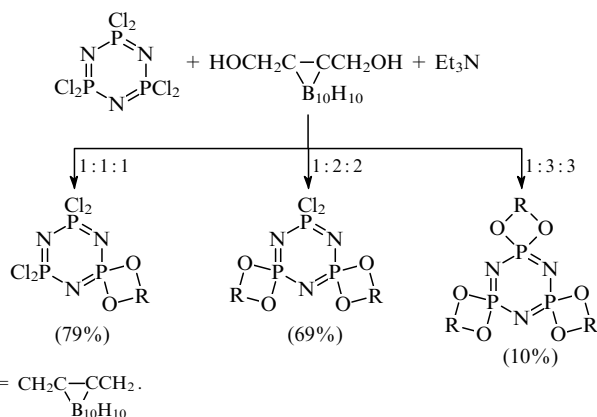


In the series of *C*-substituted derivatives, carborane-containing phosphazenes and polyphosphazenes have been synthesised.^{77–82} The reactions of hexachlorocyclotriphosphazene (HCP) with lithio-*m*-carborane and with *m*-carboranethiol in the presence of Et_3N have been described.⁷⁷

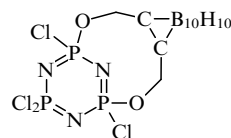


$\text{R} = \text{CB}_{10}\text{H}_{10}\text{CH}$, $\text{X} = \text{Li}$; $\text{R} = \text{SCB}_{10}\text{H}_{10}\text{CH}$, $\text{X} = \text{H}$.

The reaction of 1,2-bis(hydroxymethyl)-*o*-carborane **81** with HCP in the presence of Et_3N has resulted in the formation of spiro-compounds. The number of substituted chlorine atoms depended on the ratio of the reactants.⁸¹



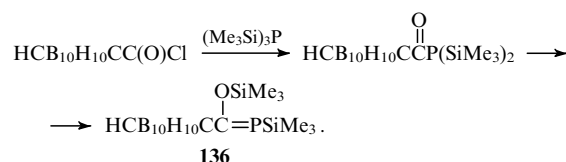
The formation of *ansa-o*-carboranylenecyclotriphosphazene has also been observed.⁸²



Synthesis of carborane-containing polyphosphazenes by the substitution of carborane-containing groups for the chlorine atoms in polychlorophosphazenes (PCP) has been reported. The reaction was accomplished by treating PCP with lithio-derivatives of *o*- and *m*-carboranes or with *m*-carboranethiol.^{77, 79} When 2 or 2.5 moles of *m*-carboranethiol, lithium *o*-carboranymethoxide or lithium *o*-carboranymethylphenoxide per mole of PCP was introduced into this reaction, products of replacement of up to 50% of the chlorine were obtained.⁷⁷

The preparation of polymeric carborane-containing phosphazenes by polymerisation of carboranypentahalodicyclopophosphazene has been patented.⁸⁰

In addition to all the carborane-containing organophosphorus compounds listed above, the first, and still the only, derivative of two-coordinate phosphorus **136** has been described. This compound was synthesised by treatment of *m*-carborane-1-carbonyl chloride with tris(trimethylsilyl)phosphine.⁸³



IV. Potential fields of application of carborane-containing organophosphorus compounds

The potential practical use of carborane derivatives is substantially restricted by their high cost. This is completely true for the carborane-containing organophosphorus compounds. Nevertheless, there are several patents dealing with practical use of these substances. First of all, this refers to carborane-containing phosphazenes and polyphosphazenes, which have been proposed as thermally stable and flame resistant materials and also as additives decreasing inflammability of polymers and paper.^{26, 29, 79, 80}

It has been reported that it is possible to use carborane-containing organophosphorus derivatives as biologically active compounds. In this respect, prospects for using these compounds in the neutron-capture therapy of cancer should be mentioned first.^{84–86}

The pesticide, gametocide and bactericide activities of these derivatives have been assayed.^{50, 55, 87–89}

Anticholine esterase activities of various esters, thioesters and selenoesters of phosphorus acids have been studied. In the case of compounds in which the carboranyl group is directly attached to the phosphorus atom, this activity is weak and is much lower than that of similar phosphorus derivatives devoid of the carboranyl groups.^{50, 87}

For derivatives of thioacids of pentavalent phosphorus in which the carboranyl group is incorporated in the ester moiety, the anticholine esterase activity has been found to be higher than that of the corresponding thioesters without carboranyl group.^{55, 88}

The pesticide properties have been tested most extensively for the 2,2-dichlorovinyl carboranylphosphonates. Weak insectoacaricide and relatively low herbicide and fungicide activities have been found.⁵⁰ These derivatives were also found to exhibit high gametocide activities. Good prospects for using them in the production of hybrid wheat seed were shown.⁵⁰

Some *o*-carboran-9-yl esters of phosphorus thioacids have been found to exhibit bactericide activities.⁸⁹

V. Conclusion

The most interesting aspect of the information given above is the properties of carborane-containing organophosphorus compounds and their comparison with the properties of similar compounds devoid of the carboranyl group.

closo-Dicarbododecaboranes are known to be electron-deficient systems with respect to substituents at the carbon atom, the strongest electron-withdrawing effect being observed in the case of the *ortho*-isomer, whereas the weakest effect being typical of the *para*-isomer. The reactivities of these compounds can also be markedly influenced by steric factors caused by the large size of the carboranyl groups.

The above factors influence most crucially reactions of those carborane-compounds in which the carboranyl group is linked directly to a trivalent phosphorus atom. The nucleophilicity of the phosphorus atom in these compounds is substantially decreased; hence, oxidation, addition of sulfur and azides, the Arbuzov and Perkow reactions, *etc.*, occur under more drastic conditions than those for conventional derivatives of trivalent phosphorus. The influence of steric factors also cannot be neglected; however, it is often difficult to distinguish it from the electronic influence. In some cases, a carboranyl group attached to a phosphorus atom can act as a pseudo-halogen atom in reactions with nucleophilic reagents, which occur with rupture of the phosphorus-carborane carbon bond.

B-Substituted carborane-containing organophosphorus compounds in which the phosphorus atom is connected to the carboranyl group *via* a sulfur or selenium bridge are more reactive than similar *C*-substituted derivatives. This is apparently due to the fact that carboranylthio- or carboranylselenio-groups exert an electron-donating effect, and the nucleophilicity of the phosphorus atom thus increases. In this case, steric factors are less significant than for *C*-substituted compounds.

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Use of electrochemical techniques to study the Langmuir – Blodgett films of redox active materials

L M Goldenberg

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Abstract. The electrochemical properties of thin films of electroactive materials formed on the surface of an electrode by the Langmuir – Blodgett (LB) technique are reviewed. Great attention has been paid to LB films of the charge-transfer materials which may form electroconductive films. This group includes tetrathiafulvalene, tetracyanoquinodimethane, dithiolate complexes of metals, fullerenes, phthalocyanines, conjugated polymers, *etc.* Also, LB films of other redox materials such as ferrocenes, metal bipyridine complexes, viologens and other electroactive LB films are comprehensively reviewed. Structure – property relationships in the experimental voltammetry of LB films and their agreement with theoretical models are examined. Specially organized structures, formed by the LB technique, for the study of the mechanism of electron transfer are of special attention. Potential applications of electroactive LB films in electrocatalysis, electrochromic displays, information storage devices and molecular electronic devices are envisaged. The bibliography includes 163 references.

I. Introduction

For a description of the Langmuir – Blodgett technique see Refs 1–5. For the electrochemical investigations, the LB films (monolayer or multilayer) are transferred onto the surface of an electrode by the conventional vertical dipping or the horizontal touching technique. Indium – tin oxide coated glass (ITO) or gold evaporated onto different supports are usually used as electrodes. Our primary interest in LB films is associated with the LB films of charge-transfer materials, which can give a mixed valence state upon oxidation or reduction. LB films of these materials can exhibit increased electrical conductivity and they may find an application in the molecular electronics (see reviews^{6–11}). Electrochemical techniques can be considered as a method of synthesis and/or method for converting these materials to the conducting state. Moreover electrochemical methods can perform this conversion in a more controllable manner because the desired level of oxidation or reduction can be achieved by passing a certain

quantity of charge. To comply with the principle of electroneutrality, oxidation or reduction is accompanied by the ingress of counter-ions. It is well known from the chemistry of conducting ion-radical salts^{7,9} that a large variety of cations and anions can be inserted in these crystals during electrochemical growth. Similarly applying electrochemical methods to LB films should yield better control of their properties. However, electrochemical doping found only limited application for LB films compared to the vast use of electrocrystallisation to grow conducting crystals and electropolymerisation to produce conjugated polymers.

The electrochemistry of LB films was reviewed by Facci¹² with emphasis on his own work with ferrocene derivatives. Previously we have also discussed the electrochemistry of LB films.¹³ In this review the field is described in more detail taking into the consideration the reports (including ours) published in the last few years.

Other electroactive LB films can serve as models to study the dependence of electrochemical properties on the film structure and the conditions of the LB transfer, *visé versa*. For example phthalocyanine LB films were investigated for their electrochromic properties, but these materials can be also electroconductive. Other potential applications for the electroactive LB films include the formation of ultrathin modified electrodes with the high density of electroactive sites and molecular organisation, which might find application as sensors, photoelectrochemical and information storage devices. LB films can serve as models for molecular rectifying properties in biological systems, electrocatalysis, study of biological membranes, *etc.*

The LB technique is able to create molecularly organised films, advantageous in the preparation of molecular electronic devices. Molecular organisation can also provide new insight on electron transfer reactions at interfaces. Self-assembly (SA) technique also produces molecularly organised films and can be considered as a complimentary approach. Generally, only one type of surface can be used in this technique (for example Au or Pt for thiols and glass or Si for chlorosilanes). This limitation creates difficulties in measuring the electrical properties. The SA technique is not universal and is often limited to monolayer formation.

II. Langmuir – Blodgett films of the charge-transfer materials

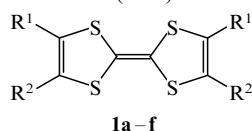
The formation of conducting LB films falls into five main groups of materials based on amphiphilic analogues of the following

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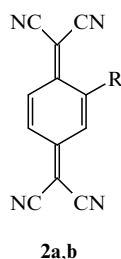
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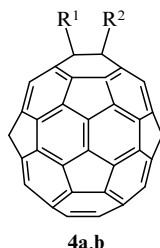
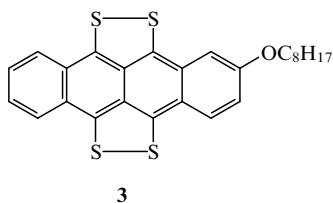
compounds: tetrathiafulvalene (TTF), tetracyanoquinodimethane (TCNQ), tetrathiotetracene (TTT), dithiolate complexes and fullerenes (**1–5**).



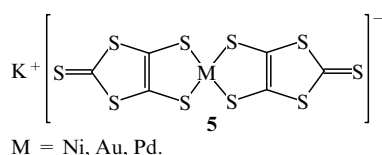
- 1a:** $R^1 = \text{H}$, $R^2 = \text{COC}_{15}\text{H}_{31}$;
1b: $R^1 = \text{H}$, $R^2 = \text{COC}_{17}\text{H}_{35}$;
1c: $R^1 + R^2 = \text{SCH}_2\text{CH}_2\text{S}$,
 $R^2 + R^2 = \text{SCH}_2\text{CH}(\text{C}_{18}\text{H}_{37})\text{S}$;
1d: $R^1 + R^2 = \text{SCH}_2\text{CH}_2\text{S}$,
 $R^2 = \text{SC}_{18}\text{H}_{37}$;
1e: $R^1 + R^2 = \text{SCH}_2\text{CH}_2\text{S}$,
 $R^2 = \text{H}$, $\text{CH}_2\text{OCOC}_{17}\text{H}_{35}$;
1f: $R^1 = \text{H}$, $R^2 = \text{H}$, $\text{CH}_2\text{OCOC}_{17}\text{H}_{35}$.



- 2a:** $R = \text{C}_{18}\text{H}_{37}$,
2b: $R = \text{C}_{12}\text{H}_{25}$.



- 4a:** $R^1 + R^2 = \text{double bond}$;
4b: $R^1 = \text{H}$, $R^2 = \text{Bu}^t$.



Chemical oxidation, usually by I_2 vapour, used to be the general method to convert the films to the mixed-valence conducting state. One of its disadvantages is that in these cases the conducting state is not stable as films loose iodine. Several attempts to use electrochemistry can be found in the literature. The electrochemical oxidation during LB film deposition was performed for a TTT derivative **3**¹⁴ using LiClO_4 subphase and for a mixture of compound **1d** and behenic acid¹⁵ using 0.002 M KI subphase. The mixed-valence state in LB film was observed spectroscopically in the latter case. Direct electrochemical oxidation of TTF LB films during deposition was suggested.¹⁵ Alternatively, one could suggest that I^- oxidation takes place under these conditions and then I_3^- oxidises TTF chemically. This oxidation on a live electrode (as well as post-deposition oxidation) conserves the ordering in the LB film in contrast to I_2 vapour oxidation which yields a disordered structure.¹⁴ Recently we deposited LB layers of Ni complex **5** with tetrabutylammonium cation onto the electrode with a gap of 30–50 μm under constant current.¹⁶ We were the first to report electrical conductivity ($10^{-3} \text{ S cm}^{-1}$) using this approach.

Deposition under constant potential was applied to control the adsorption of malachite green, dissolved in the subphase, into LB films of TCNQ derivative **2b**.¹⁷ The adsorption was assigned to the electrochemical reduction of **2b** and the formation of charge-transfer complex between reduced **2b** and malachite green during LB transfer onto ITO electrodes.

It can be suggested that compact LB films may be oxidised or reduced during the process of electrochemical LB deposition, while a similar electrochemical reaction might be inhibited in the preformed LB films.

Postoxidation of preformed LB films is more widely used. To study the electrochemical properties of LB films voltammetric methods with linear sweep of potential, particularly cyclic voltammetry, are usually employed. The theoretically expected response for the surface electrochemical reaction in this technique is a symmetrical cyclic voltammogram (CV) (without peak separation) and a peak half width of ca. 90 mV for the one electron transfer. The best (closer to theoretically expected) stable CV

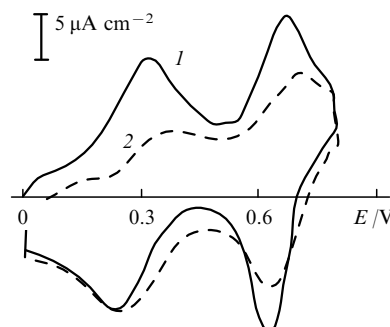


Figure 1. CV of LB film of mixture of **1f** and 23% molar icosanoic acid on ITO glass, 0.2 M HClO_4 solution. Potentials vs. SCE; (1) monolayer, (2) 5 layers, $v = 200 \text{ mV s}^{-1}$.

response between LB films of the TTF derivatives **1** was registered for the derivative **1f** (Fig. 1).[†] The deviation from the theoretically expected response is manifested in the peak broadening and peak separation. It should be noted that despite the compact structure (the low molecular area¹⁸), the shape of the CV response for the multilayer film was similar to the response of the monolayer. As expected for the surface electrochemical reaction for both monolayer and multilayer films the peak current was proportional to the scan rate. However, the electroactivity of monolayer films was lower than that calculated from the LB transfer and decreased further in the case of multilayer films (Fig. 1).

It was shown spectroelectrochemically^{19,20} that even compact films of TTF derivatives **1a** and **1b** could be oxidised in aqueous electrolyte forming a mixed-valence state. The study of films of **1a** (molecular area close to 0.2 nm^2 , corresponding to the cross-section of the alkyl chain) by cyclic voltammetry has shown that the redox process is quite slow and the oxidation is controlled by diffusion of electrolyte ions through a highly hydrophobic film.¹⁹ For several layers, CV response was highly distorted due to hindered diffusion of ions. Similar behaviour for the LB films of fullerene derivative **4b**²¹ is shown in Fig. 2. Three diffusion controlled reversible or quasi-reversible reduction steps (Fig. 2a) were observed for monolayer film. The CV response was sug-

[†] L M Goldenberg, R Andreu, M Saviron, A J Moore, J Garin, M R Bryce, M C Petty, unpublished results.

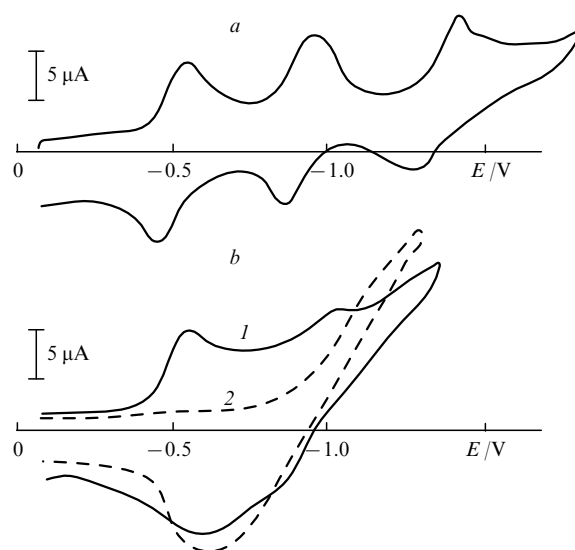


Figure 2. CV of a monolayer film (a) and multilayer (b) of **4b** on ITO glass in 0.1 M Bu_4NPF_6 -acetonitrile. Potentials vs. SCE, $v = 10 \text{ mV s}^{-1}$; (1) 3 layers, (2) 11 layers.

gested to be limited by the ion diffusion through well ordered hydrophobic film. The CV shape became severely distorted for multilayer films (Fig. 2b).[‡]

The study of CV response of LB films of other TTF derivatives **1c**,^e ^{18,22} has shown a large influence of the LB film organisation on the electrochemical properties. Films of **1c** have been formed at quite low surface pressure and were not well organised as shown by IR spectroscopy.²² The films possibly contained a sufficient amount of the defects and short S...S contacts between TTF molecules. As a result CV response was unstable, the oxidation peak was shifted anodically and CV response was not changed in multilayer films (Fig. 3). Unstable CV response with peak splitting was also observed for LB films of material **1e**.¹⁸ The more amphiphilic nature of this material resulted in better film properties. Low electrochemical activity of multilayer films was observed possibly due to a more compact structure.¹⁸ The study of the electroactivity of LB films of a number of TTF derivatives^{23–25} resulted in unstable CV responses, often complicated with additional peaks.

Tiecke and co-workers were able to observe a well developed

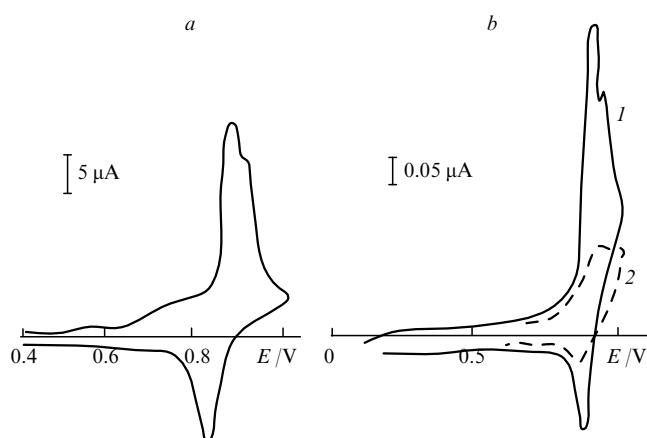


Figure 3. CV of LB film of mixture of **1c** and 20 mol.% stearic acid on ITO glass, saturated KCl solution.²² Potentials vs. Ag/AgCl; (a): 5 layers, $v = 50 \text{ mV s}^{-1}$, (b): (1) — monolayer, $v = 25 \text{ mV s}^{-1}$, (2) — second scan.

CV response for the multilayer films of **3**.^{14,26,27} It is remarkable, that very thick films (80 layers) exhibited the undistorted response,²⁸ when the films were deposited in the form of radical-cation salt formed on a subphase containing dodecyl sulfate anions. Radical-cation salt formation led to a 70% increase in the molecular area and, possibly, to the formation of the channels for the ion transport. The presence of ions inside LB films may also facilitate the electrochemical reaction.

Nakamura and co-workers²⁹ measured conductivity up to $10^{-3} \text{ S cm}^{-1}$ for LB films of derivative **2a** (15–51 layers) after electrochemical doping at -0.1 V vs. SCE . CV of these films demonstrated large peak separation (about 0.4 V) and prepeaks. However, CVs were improved after electroactive compound in the films was diluted by methyl arachidate probably due to a decrease of repulsive interaction between electroactive sites as predicted by theory.³⁰

LB films of complexes **5**, deposited by the horizontal lifting method,^{31–41} were doped electrochemically. A conductivity as high as $25\text{--}50 \text{ S cm}^{-1}$ for Au complex with tridecylmethylammonium cation (1:1 mixture with icosanoic acid, 20 layers) and in the range of $3 \times 10^{-4}\text{--}5 \text{ S cm}^{-1}$ for other complexes of Ni and Pd was obtained after the constant current oxidation of the LB films

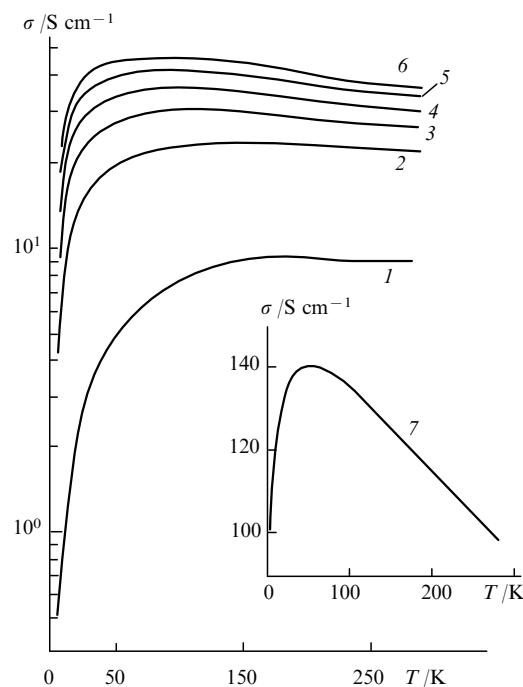


Figure 4. Conductivity as function of temperature for LB films of Au-complex **5** (1:1 mixture with icosanoic acid, 20 layers, after the electrochemical doping) under 0 (1), 2.7 (2), 7 (3), 9.5 (4), 10.9 (5), 11.1 (6) and 9.8 (7) kbar.⁴¹

in LiClO_4 aqueous electrolyte.^{31,32–37} Quasi-metallic character of the conductivity–temperature dependence^{31,32,34–37} (Fig. 4) and the increase of the conductivity with pressure^{38,41} were registered for Au complex. ESR³³ and thermoelectric power^{35–37} measurements also indicated the metallic nature of the films. Very high electrical conductivity of 140 S cm^{-1} was registered at 51 K and 11 kbar.⁴¹

It was previously shown^{37,40,41} that the conductivity was unstable (3-fold decrease in 3 days) and only freshly prepared films showed the metallic conductivity–temperature dependence. In contrast, low-angle X-ray scattering data and thermoelectric power were stable.⁴⁰ All these high conductivity values were calculated assuming the layer thickness of 3 nm^{31,32,41} despite the AFM study,³⁹ which revealed plate-like crystallites with a height of about 18 nm. The blurring of the outline of the crystallites was clearly seen after the electrochemical oxidation. The morphological change was accompanied by an increase of the d -spacing from 1.9 to 2.7 nm.³⁵ The value of the d -spacing in as-deposited film was ascribed to the interplanar distance of Au complex crystallites as the same value was obtained by X-ray structure analysis of a single crystal.^{35,39} This study has been repeated in more detail later³⁴ and the d -spacing of 1.92 nm for as-deposited samples was confirmed. However, this weak pattern was accompanied by stronger peaks corresponding to the d -spacing of 4.88 and 4.43 nm. The latter values were ascribed to the icosanoic acid matrix (Y type bilayer). After the electrochemical doping, a new peak corresponding to the d -spacing of 3.48 nm appeared. It is unclear how the value of 3.48 nm is correlated to an earlier observed value of 2.7 nm.³⁵ Using molecular structure simulation, it was suggested⁴⁰ that the direction of the longest axis in this complex is almost parallel to the surface of the support. In doped films, molecules of the complex are dimerised along the direction normal to the surface. Molecular resolution with the parallelepiped pattern, specified by $1.06 \times 1.31 \text{ nm}^2$, corresponding to molecular area of complex, was observed in AFM images of the monolayer film.⁴⁰ It should be noted, that in this report, AFM was used only for as-deposited samples and possible formation of crystallites was not discussed.⁴⁰ Experimentally observed molec-

[‡] L M Goldenberg, G Williams, M R Bryce, A P Monkman, M C Petty, A Hirsch, A Soi, unpublished results.

ular area was 0.28 nm^2 (Ref. 35), which suggests the multilayer or crystallite formation on the water surface.

Recently we studied a similar Ni complex **5** with the octadecylpyridinium cation.^{42,43} Both single layer and multilayer films were electroactive with CV peak intensity proportional to the number of layers.⁴³ LB films were built-up under different conditions resulting in an electrical conductivity difference of a few orders of magnitude.⁴² Electrochemistry was found to be useful for determining the difference between these films. The CV response revealed that the same chemical compound was transferred on the solid substrate despite the difference in conducting properties. However, film structure influenced the electroactivity and peak separation (indication of difference in electrochemical kinetics). This suggests that the LB films built-up from the true monolayer (non-conducting films) exhibited slower electrochemical kinetics, because according to schematic structure of the film⁴² the molecules of electroactive complex are buried among the hydrophobic chains and are farther from the electrode surface. Electrochemical doping at constant potential of the LB film deposited onto the interdigitated electrode (Fig. 5) exhibited peak shaped current transient (time dependence of current at constant potential). This may be explained by an increase in the effective electrode area due to nucleation of the conducting phase between the fingers of the interdigitated electrode until the film achieves maximum conducting state. The charge consumed in this process corresponds to roughly half of the material being oxidised and consequently to the mixed-valence state. The conductivity value of up to $3 \times 10^{-2} \text{ S cm}^{-1}$ was registered either with KCl or LiClO_4 electrolytes. The conductivity values and activation energy for these films were similar to ones for the films doped with iodine vapours.^{42,43} It should be noted that lower conductivity for these films compared with Au and Pd complexes, studied by Matsumoto group (see above), can be partially explained by using layer thickness measured by profilometry [about 30 nm (Ref. 42)] to calculate the conductivity value, but not the assumed layer thickness of 3 nm.^{31,32,41}

The similar approach was applied to obtain conductive LB

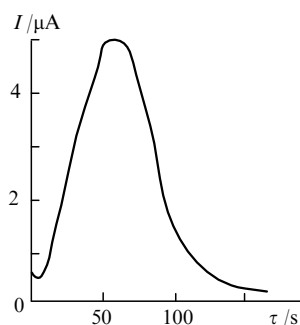


Figure 5. Current transient after application of a potential step for LB film of Ni complex **5** on interdigitated electrode in 3 M KCl solution.⁴³

films from the mixtures of tetrabutylammonium Ni complex **5** and tricosanoic acid.¹⁶ LB films were oxidised at constant potential or constant current in the different electrolyte solutions. In-plane dc conductivity up to $10^{-2} \text{ S cm}^{-1}$ was registered after the electrochemical doping in different electrolytes or chemical doping by iodine vapours.¹⁶ It should be mentioned that samples, doped electrochemically in LiClO_4 or KI electrolyte or by iodine vapour, were more stable than the samples doped electrochemically in KCl or Bu_4NBr electrolytes. The CV response in all electrolytes studied was similar to the one registered for LB films of the amphiphilic Ni complex.⁴² The reversible rapid changes in the visible spectrum were observed under the application of the potential to the LB films (Fig. 6).

Bard and co-workers^{44–46} studied the electrochemical behaviour of LB films of C_{60} **4a**. The first two reduction waves were

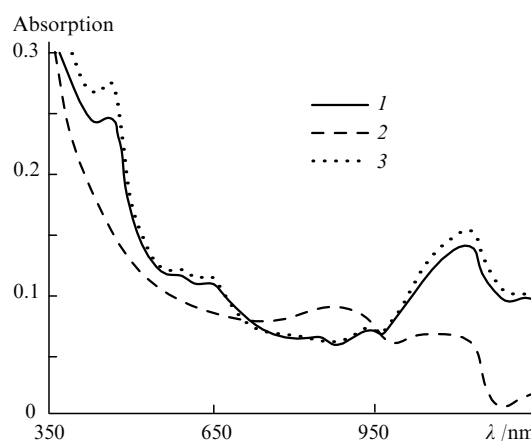


Figure 6. Spectroelectrochemistry upon oxidation of tetrabutylammonium Ni complex **5** (40 mol. % of tricosanoic acid) on ITO electrode, 0.5 M Bu_4NBr aqueous solution.

Potentials vs. Ag wire; (1) open circuit, (2) 1 V, (3) -0.3 V .¹⁶

studied in order to avoid dissolution of films. Most probably these films were not true monolayers. Peak current increased and peak half width decreased with the increase of surface pressure used for film deposition. Peak separation was about 210 mV for lower surface pressure and even at higher surface pressure this value was smaller than that for the cast films.

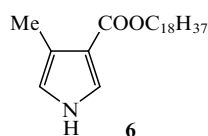
Photoelectrochemical properties of the LB films of C_{60} **4a** and pyrrolidinium derivatives of C_{60} were investigated.⁴⁷ The highest photocurrent quantum yield was observed for the derivative with an electron-donating *o*- Me_2NPh group attached to the pyrrolidine ring.

In conclusion, the electrochemical methods can be used for the fabrication of conducting LB films of charge-transfer materials. The electrochemical doping can be realised either during LB film transfer using the subphase as an electrolyte or after LB deposition for already fabricated films. As a result, highly ordered conducting films can be obtained and different counter-ions can be introduced into the LB films. However, further investigations are necessary to elucidate the counter-ion – property relationship. It should be emphasised that very high conductivity of 50 S cm^{-1} , with partially metallic temperature dependence of conductivity, has been obtained using electrochemical technique.

III. Conjugated polymers

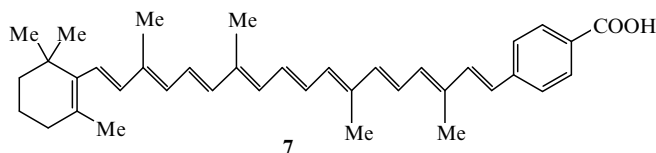
The use of electrochemistry for conducting polymer LB films has been very limited despite the number of such polymeric films prepared to date (see review⁴⁸). The successful application of the electrochemical polymerisation for LB films of amphiphilic pyrrole **6**^{49–51} is one of the few reported. A short length (several mm) of the electrode covered with LB multilayer film is dipped in $\text{LiClO}_4/\text{acetonitrile}$ electrolyte and a coloured area appears when polymerisation proceeds under an applied potential. Then the covered with polypyrrole part of electrode served as a connecting lead for the rest of the LB film.⁸ Multilayer polypyrrole films obtained by this method had highly anisotropic conductivity ($10^{-1} \text{ S cm}^{-1}$ for the direction parallel to electrode surface and $10^{-11} \text{ S cm}^{-1}$ for the direction normal to electrode surface). Low angle X-ray scattering also showed that the part of polypyrrole film which was not immersed in the electrolyte solution kept a highly ordered structure. Thus, this method allows synthesis of highly ordered polypyrrole films, which are impossible to obtain by electropolymerisation of the monomer in solution.

§ It is important that electropolymerisation could not be carried out in aqueous electrolyte, possibly due to hindered diffusion of the water molecules in hydrophobic multilayer films.

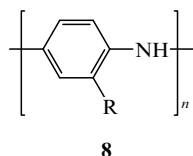


Electrically conducting fine lines of polypyrrole in a matrix of icosanoic acid were fabricated by electrochemical polymerisation during LB film deposition.⁵² Pyrrole and icosanoic acid were spread on a LiClO₄ subphase and transfer onto ITO electrode was performed by application of 10 V between the moving ITO electrode and the Pt counter electrode. The resulting low conductivity of the film ($8 \times 10^{-5} \text{ S cm}^{-1}$) may possibly be ascribed to the fact that the concentration of pyrrole in the matrix is low since most of pyrrole would go into the subphase.

Carotenoids are polyenes and are thus related to the simplest conjugated polymer, polyacetylene. Their importance in photosynthesis and possible involvement as photoreceptors are well known. The photoelectrochemistry of LB films of carotenoid **7** was studied on ITO electrodes.⁵³ For films up to five layers thick, the photocurrent was linear with the number of layers. This suggests that there is efficient charge and possibly energy transport between monolayers.



We studied single layer LB films of polyaniline **8** with a thickness of about 6 nm.⁵⁴



We showed that the use of the LB technique for film formation resulted in the improved electrochemical properties (Fig. 7), comparable with those of the best electrochemically polymerised films (high ratio of first oxidation peak current to plateau current). As expected for the surface electrochemical reaction the

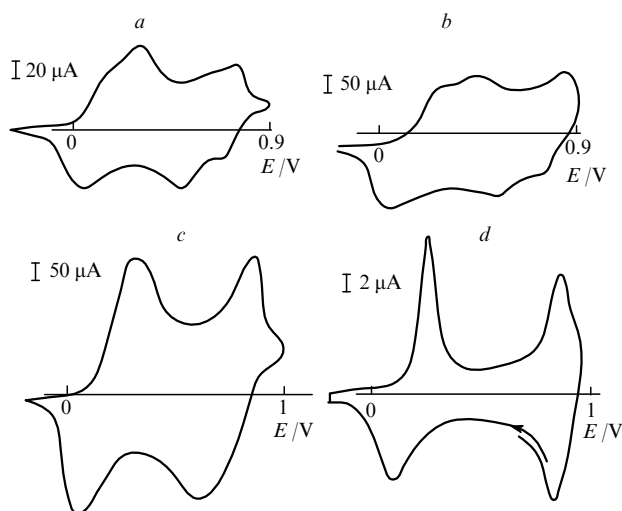
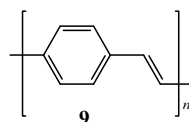


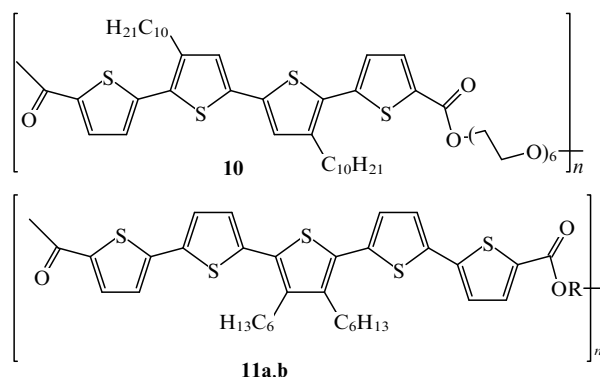
Figure 7. CVs of polyaniline **8** on ITO glass in 1 M HCl, $v = 50 \text{ mV s}^{-1}$.⁵⁴ Potentials vs. Ag/AgCl; (a) dip coated film, (b) spin coated film, (c) spin coated film after storage in water, (d) one layer LB film.

peak current was proportional to the scan rate. CV and spectroscopy have shown that LB films are reversibly oxidised (possibly by oxygen) during transfer onto the electrodes. The study of multilayer assemblies of polyaniline⁵⁵ resulted in broad peak CV which were similar to those observed by us for spin-coated films (Fig. 7⁵⁴). The distortion of the CV was attributed to slow electron transfer. In the light of a report⁵⁶ of very fast redox reaction in polyaniline we believe that hindered ion-diffusion through the thick film, but not slow electrochemical kinetics, is responsible for the observed behaviour. To improve film forming properties LB films were produced from polyaniline doped by amphiphilic acids.⁵⁷ A CV response with low peak/plateau current ratio was registered. The films of some substituted polyanilines^{57–60} exhibited less resolved CVs compared to the parent polyaniline. Three redox steps, accompanied by an electrochromic effect, could be observed for an alkoxy-substituted polyaniline derivative.⁵⁸ A comparison of different film forming techniques (electropolymerisation, spin-coating and LB technique) for poly(*o*-ethoxyaniline) showed that the LB technique was not the best in this case (broad peaks on CV).⁶⁰

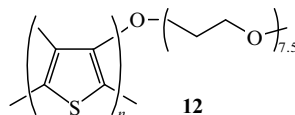
A CV response with two broad peaks was observed for poly(*p*-phenylenevinylene) **9** films, which were obtained by vacuum heat treatment of a LB film of the precursor polymer.⁶¹



Recently we studied electrochemical properties of LB films of substituted polythiophene oligomers **10**, **11** and alkoxy-substituted polythiophene **12**.⁶²



R = $-(\text{CH}_2\text{CH}_2\text{O})_6-$ (a), $-(\text{CH}_2)_{10}\text{O}-$ (b)



Oligomers of polythiophene exhibited facile electrochemical behaviour with narrow symmetrical peaks on the CV (Fig. 8). Aggregated films of polythiophene **12**, transferred under special conditions, demonstrated molecular recognition of alkali metal cations (the anodic shift of peak potential upon the addition of metal ions), similar to cast films (Fig. 9).[†]

LB films of oligoimides (**13a–d**) closely related to conducting polymers have been obtained by Miller *et al.*^{63, 64}

[†]L M Goldenberg, M Leclerc, M C Petty, unpublished results.

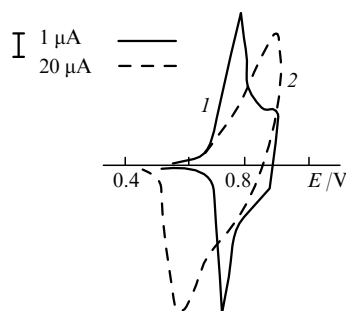


Figure 8. CV of 7-layer LB film of oligomer **10** in 0.2 M Bu₄NBF₄-acetonitrile. Potentials vs. Fc/Fc⁺; (1) 25 mV s⁻¹, (2) 1 V s⁻¹.

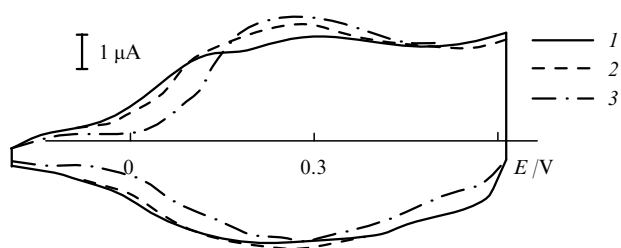


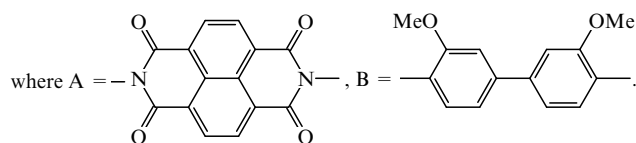
Figure 9. CV of LB films of polythiophene **12** (3 layers) in 0.2 M Bu₄NBF₄-acetonitrile. Potentials vs. Fc/Fc⁺, $\nu = 50$ mV s⁻¹; (1) without Na⁺, (2) [Na⁺] = 1.59×10^{-3} M, (3) [Na⁺] = 7.49×10^{-3} M.

13a: HSPH-A-B-A-B-A-B-A-B,

13b: -O₃SPh-A-B-A-PhSO₃-,

13c: HO₂CPh-A-B-A-PhCO₂H,

13d: B-A-B-A-B-A-B-A-B-A-B,



These imides are able to form *p*-dimers in solution and stacks in electroprecipitated conducting films. The CV of film **13b** shows a reduction peak and two reoxidation peaks (Fig. 10).⁶³ The films were fully electroactive up to at least 8 layers. Peak current was proportional to scan rate. Even the cathodic peak half width (70–120 mV depending on compound) was rather close to the theoretically expected value (90 mV) for a one-electron surface reaction. Grazing angle IR spectra have shown that the oligomer molecules were oriented with the long axis roughly parallel to electrode surface (tilt angle $\sim 15^\circ$), but after electrochemical cycling the tilt angle increases to $\sim 35^\circ$. That is similar to the value in isotropically oriented evaporated films and thus electrochemical cycling disrupts the original organisation⁶³ in contrast to the films of **3**¹⁴ and polypyrrole **6**.⁴⁹ The doubling of the reoxidation peak and large peak separation can be explained by thermodynamic stabilisation of the radical-anion in the LB films due to possible formation of dimers or stacks, which oligoimides form in solution.⁶⁴ It can also be explained by sufficiently negative interaction energy in a theoretical model.³⁰ That suggests that reduced LB films of **3a–d** could be anisotropic conductors.

Compound **13a** was studied in three possible forms: LB films, an evaporated film and an SA monolayer⁶³ (Fig. 10 for SA and LB films). The cathodic peak was broader in the evaporated film compared to LB film and SA film. The SA film exhibits only one reoxidation peak, which suggests that interactions between molecules are weaker.

Thus, LB technique allows to fabricate high quality conjugated polymer electrodes. Conducting films with the high

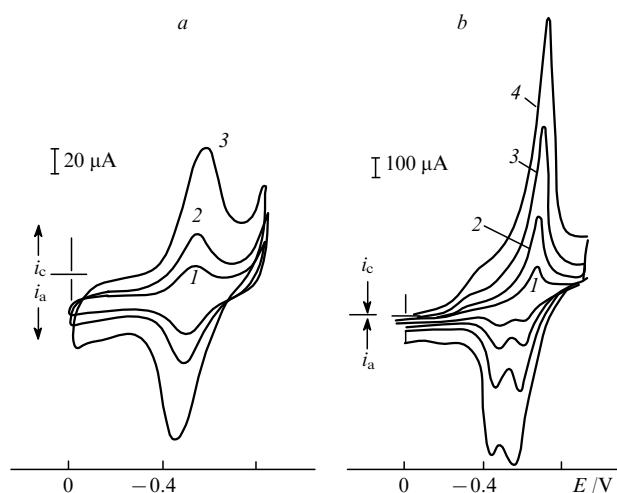


Figure 10. CVs of **13a** films.⁶³

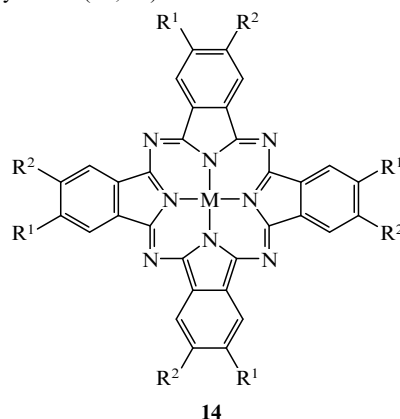
Potentials vs. SCE; (a) SA film at 100 (1), 200 (2) and 500 (3) mV s⁻¹ in 0.1 M Ph₄NBF₄-DMF, (b) 6 layers LB film at 20 (1), 50 (2), 100 (3) and 200 (4) mV s⁻¹ in 0.1 M aqueous BaCl₂.

anisotropy of the electrical conductivity were obtained. Electro-polymerisation on the water surface in an LB trough during the film transfer is of interest. Many of conjugated polymers are used for the fabrication of light emitting diodes. Electrochemical light emitting cells can possess the improved characteristics compared to the conventional light emitting diodes. Recently, LB films of conjugated polymers were employed as emitting layers of the light emitting diodes. The electrochemical properties of the films should be further investigated in order to use them in electrochemical light emitting cells.

IV. Coordination compounds

1. Phthalocyanines and related compounds

The main interest in the electrochemical properties of the phthalocyanines (Pc, **14**)



has been related to their electrochromic properties. The LB technique was used as an alternative method to casting for the fabrication of electrochromic films. Electrochromic properties were first reported for LB films of unsubstituted monophthalocyanine;⁶⁵ CV with broad peaks corresponding to a transition from green to red form under oxidation and to purple form under reduction was registered. The detailed paper reported the electrochemical study of alkyloxy-substituted diphtalocyanine Lu⁶⁶ and LB films showed a one-electron reversible oxidation and a one-electron reversible reduction corresponding to a transition from green to orange and blue forms, respectively. The CV response of multilayers was not distorted and well defined peaks were observed. The electroactivity of films under oxidation

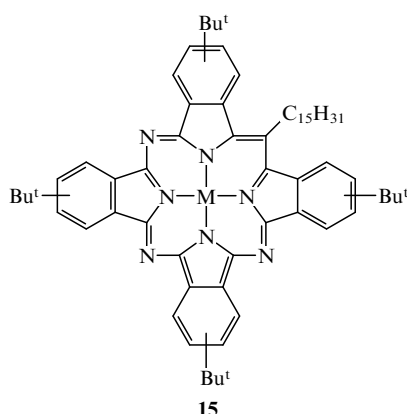
corresponds only to 30%–50% of the amount of the deposited material and peak currents are neither proportional to scan rate nor to square root of scan rate. The CV for this compound shows a distinctive diffusion tail. Peak separation was highly dependent on the anion of the electrolyte. Thus, the electrochemical response was at least partially controlled by the diffusion of counter-ions.

The electrochemical properties of a variety of phthalocyanine LB films have been studied.^{65–82} YPc₂ LB films,⁷⁵ mixed with icosanoic acid, showed well developed CV response with peak current proportional to the scan rate. In contrast to the evaporated or cast films, the CV response for LB films was stable upon potential cycling. Three distinct colours (blue, green and red) were observed within the potential range of 1 V. LB films of PrPc₂⁷⁹ also showed better resolved and stable CV response compared to the cast films. Four colour changes were attained and the absorbance decreased by only 35% after 10⁵ electrochromic cycles.

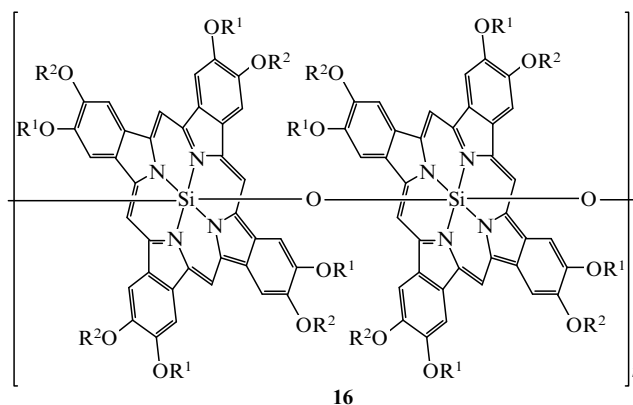
The electrochemical properties of the LB films formed by Cu and Ni monophthalocyanine substituted with short branched chains were studied.⁸¹ Three surface confined redox transitions (electroactivity of about 30%) were observed in acetonitrile solution; electrochromic effect was noted in a 51 layer film. However, the electrochromic response was not stable, particularly in thicker films, due to desorption of the LB film upon potential cycling.

The multilayer assemblies of asymmetrical tetraphenyl substituted LuPc₂ exhibited two or three redox steps,⁸⁰ accompanied by colour changes from blue to green and from blue to red. The spectral peaks were better resolved and the electrochromism was more stable in the LB films than in the cast films.⁸⁰

The first example of phthalocyanine LB films, in which phthalocyanine molecules were not aggregated, has been studied by Lever and co-workers.⁷⁸ Fe bears two long-chain ligands in FePc and these ligands prevent aggregation.⁷⁸ The bilayer film was not electroactive in an aqueous electrolyte. This may be due to blocking of the counterion diffusion by the long chains.⁷⁸ In contrast, well developed electrochemical response was observed for the randomly oriented cast film, indicating a high level of organisation in the LB films. The same group⁷⁷ reported on the assembly of LB films of a new phthalocyanine derivative **15**. A surface electrochemical reaction response with broad peaks was observed at low scan rate for a 10 layer LB film of this amphiphilic Pc.



Recently Wegner and co-workers⁷⁶ reported on the CV and spectroelectrochemical characterisation of highly ordered LB multilayers of 'hairy-rod' polyphthalocyaninosiloxanes **16**. The films showed notable stability in aqueous and nonaqueous electrolytes. Up to 100% one-electron oxidation per phthalocyanine ring was achieved at 1 V vs. Ag/AgCl.



R¹ = Me, R² = C₈H₁₇, C₆H₁₂CH = CH₂

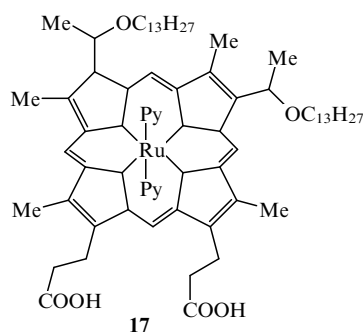
Some of the phthalocyanine LB films showed CVs with peak intensity proportional to the square root of scan rate whose shapes were rather close to a diffusion controlled wave.^{72, 74} In general, we can state that electrochemistry in Pc LB films is quite facile. Multilayer films can be easily oxidised and reduced and improved electrochemical properties were observed compared to cast films in some cases.^{69, 70, 75} An explanation of relatively facile redox reaction in multilayers is that the phthalocyanine ring is large compared to the alkyl tail projected area and thus even in the solid condensed state enough empty space and channels can be present in LB films to allow ion transport.

Electrochromic devices based on LB films exhibit low response time and improved stability upon potential cycling. Bearing in mind that chemical oxidation can be used for the doping to create electroconducting materials (see review¹⁰) and the quite facile electrochemistry of these films, electrochemical techniques can be used for producing electroconducting phthalocyanine LB films.

Porphyrin derivatives were studied with an eye to their biological properties as compounds providing electron transfer in such important biological processes as photosynthesis.

Cytochrome *c* was incorporated in an LB film of phospholipid to prevent denaturation on the electrode surface.⁸³ CV was simulated according to the surface reaction model to yield an estimate of the first-order rate constant of 2 s⁻¹. Such a small value of the rate constant was explained by either a large separation of redox centres from the electrode or nonoptimised orientation of cytochrome *c*.

LB films of Ru hematoporphyrin **17** were studied by CV.⁸⁴



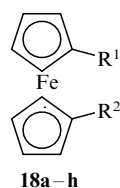
Laviron⁸⁵ presented the theoretical treatment for a surface electrochemical reaction in multilayer modified electrodes. Daifuku *et al.*⁸⁶ extended this treatment to a monolayer. Ueyama *et al.*⁸⁴ suggested a model for Z-type multilayer LB films (when the electroactive heads in all the layers are oriented in the electrode direction). Films were transferred in a solid condensed state with molecular area of 0.83 nm². Even at slow scan rates the peak separation for CVs in the monolayer was 90 mV, which was attributed to rearrangement of porphyrin rings during the redox reaction.⁸⁴ The plots of peak potential vs. ln of scan rate were

linear, starting from about 10 V s^{-1} (irreversible electrochemical reaction), and slopes of these plots gave values of the transfer coefficient of 0.32 and 0.42 for anodic and cathodic reactions respectively. First-order rate constants of 51.1 and 21.1 s^{-1} were obtained for the cathodic and anodic reactions respectively. The simulated and experimental voltammograms for the cathodic wave were not in good agreement, indicating some deviation from the Daifuku model. Two- and three-layer Z-type LB films exhibited complete electroactivity. The peak separation and peak half width increased with an increase of the scan rate. The charge, consumed upon electrochemical cycling, was constant at relatively low scan rates and decreased at high scan rates. This suggests that not all porphyrin rings participated in the electrochemical reaction at higher scan rates. Comparison of experimental and simulated voltammograms⁸⁴ yielded a pseudo-first-order rate constant for interlayer electron transfer of 256 and 128 s^{-1} (and the electron diffusion coefficient of 1.6×10^{-11} and $0.8 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$) for anodic and cathodic reactions respectively. At higher scan rates (above 12.8 V s^{-1}) disagreement was observed between simulated and experimental voltammograms, which was attributed to slow counter ion transport. In our opinion even the CV at slow scan rate reveals some diffusional tailing.

Thus, LB films of porphyrins can be a good experimental model for the development of a theory of surface electrochemical reaction.

2. Ferrocene derivatives

Bilewicz and Majda incorporated BuFc **18c** in a passivating $\text{C}_{18}\text{H}_{37}\text{SH}/\text{C}_{18}\text{H}_{37}\text{OH}$ mixed monolayer on a gold electrode⁸⁷ and showed that Fc in the matrix was entirely electroactive.



- 18a:** $\text{R}^1 = \text{R}^2 = \text{CONHC}_{18}\text{H}_{37}$;
18b: $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{CONHC}_{18}\text{H}_{37}$;
18c: $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{Bu}$;
18d: $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{CH}_2^+\text{NMe}_2\text{C}_{18}\text{H}_{37}$;
18e: $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{C}_{15}\text{H}_{30}\text{COOH}$;
18f: $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{COCH}_2\text{CH}_2\text{COFc}$ ($\text{Fc} = \text{C}_5\text{H}_5\text{FeC}_5\text{H}_4$);
18g: $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{C}(\text{O})\text{OCH}_2\text{CH}_2\text{S}-\text{TTF}$;
18h: $\text{R}^1 = \text{R}^2 = \text{C}(\text{O})\text{OCH}_2\text{CH}_2\text{S}-\text{TTF}$.

A well developed CV with high peak separation about 0.4 V (possibly due to IR drop) was obtained for a densely packed (mean molecular area 0.26 nm^2) eleven layer LB film of an amphiphilic Fc derivative **18b**.⁸⁸

For the Fc derivative **18d** it was shown that the surface pressure used for LB film deposition (and consequently the packing density) did not influence the electrochemical properties.⁸⁹ The CV response corresponded to the surface reaction model with a low peak separation (20–30 mV) and a peak current proportional to the scan rate. An electroactivity fraction of around 55%–80% was observed. Possible reasons for such behaviour could be partial monolayer dissolution, incomplete physical contact of Fc sites with the electrode, reorientation of the film after immersion in the electrolyte solution, hindering of counter ion transport by hydrophobic tails and uncertainty in charge calculation due to high background current. The highest electroactivity (about 80%) was obtained for a surface pressure of 22 mN m^{-1} (mean molecular area 0.37 nm^2). The formal potential for LB film was 0.14 V more positive than for the soluble Fc analogue. It was interpreted as the Fc moiety being more strongly adsorbed to the gold surface than the ferrocenium moiety and the surface wave may be regarded as an adsorption postwave. An SA monolayer of the same compound showed much narrower peaks

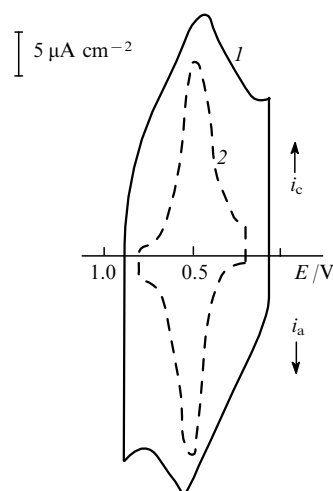
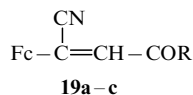


Figure 11. CVs of **18d** monolayer in 1 M H_2SO_4 . Potentials vs. SSCE; (1) LB monolayer on Au electrode, (2) SA on Pt/I electrode.⁸⁹

(Fig. 11). Broadness of CVs for LB monolayers have been attributed to repulsive intermolecular interaction according to theory.⁹⁰

There is a wide variation ($0.2\text{--}0.55 \text{ nm}^2$) for reported molecular areas for amphiphilic Fc compounds.⁹¹ The cross-sections of the Fc moiety were determined using molecular modelling to be around 0.5 nm^2 .^{12,91} This value should determine the limiting molecular area for a true monolayer. The staggering of Fc heads is usually suggested¹² in the cases when lower values ($0.2\text{--}0.3 \text{ nm}^2$) have been registered.

Recently we investigated cyanovinyl Fc derivatives **19**:⁹²



$\text{R} = \text{NHC}_{16}\text{H}_{33}$ (**a**), $\text{OC}_{18}\text{H}_{37}$ (**b**), O-cholesteryl (**c**).

The change of the surface pressure–molecular area isotherm with the time that the Langmuir layer was left on the subphase surface before compression is shown in Fig. 12. The monolayer organisation undergoes change from the staggering of Fc heads to the true monolayer. This process can be monitored electrochemi-

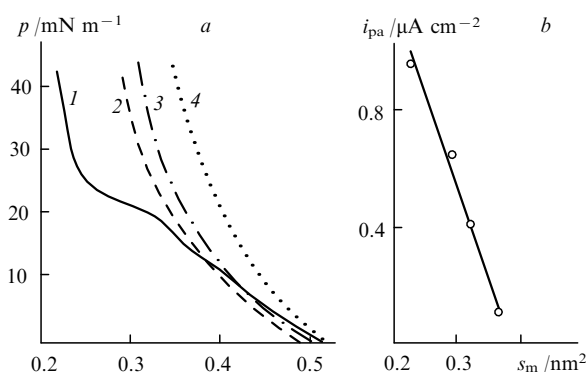


Figure 12. The change of surface pressure vs. area per molecule isotherm for compound **19a** with time, monolayer was left on the subphase surface before compression (*a*) and a plot of anodic peak current vs. molecular area at the dipping pressure (35 mN m^{-1}) for monolayers transferred onto ITO electrode after the floating film was left on the subphase surface for different lengths of time before compression (*b*); min: (1) 10; (2) 20; (3) 35; (4) 120.⁹²

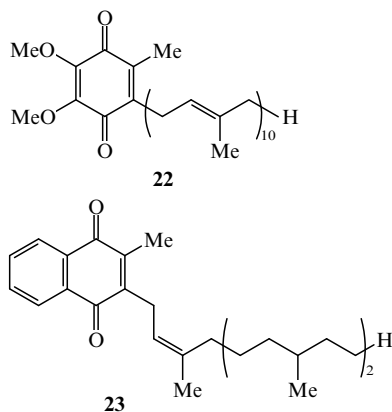
Figure 13. CVs illustrating the catalytic oxidation of Fe^{2+} by monolayer of **21a** on SnO_2 electrode in 0.18 M H_2SO_4 . Potentials vs. SCE; $v = 111 \text{ mV s}^{-1}$; (1) LB monolayer, (2) the same with 0.1 M Fe^{2+} , (3) bare SnO_2 electrode with Fe^{2+} .⁹⁵

Electroactive coverage was constant, corresponding to a limiting molecular area in the isotherm surface pressure *vs.* molecular area. An elegant experiment has shown that the monolayer was expanded to the limiting molecular area (owing to repulsive interaction between surfactant molecules) after reimmersion in electrolyte solution. An ITO electrode with a monolayer of **21c** deposited on one half was immersed in electrolyte solution, then dried and another part, where monolayer was not deposited, reimmersed. This part of electrode showed a CV response for the Ru complex. Only the inner monolayer was electroactive in the 2- and 3-layer Y-type LB films. However, a Z-type multilayer, deposited by horizontal lifting technique, showed a CV response which increased with the number of layers.⁹⁹

Thus, LB films of metal complexes (Fc, *etc.*) serve as a good model for the study of the relationship between film transfer conditions and electrochemical properties and for the development of a theory of the surface electrochemical reaction.

V. Miscellaneous materials

Amphiphilic quinone derivatives, coenzyme Q **22** and vitamin K₁ **23**, can be incorporated at a low concentration in a mixed C₁₈H₃₇SH/C₁₈H₃₇OH monolayer.^{87, 100, 101}



These quinone derivatives show complete electroactivity with a nice surface wave response and low capacitive background due to the densely packed C₁₈H₃₇SH/C₁₈H₃₇OH monolayer, enabling low quinone concentrations in the monolayer to be detected. At the surface concentration of **22** below 10⁻¹⁵ mol cm⁻² electrochemistry at single molecule 'gate sites' has been registered.¹⁰¹ These monolayers behave as an array of individually addressed 1 nm diameter disc microelectrodes. An apparent heterogeneous rate constant for the solution redox probe Ru(NH₃)₆^{3+/2+} as high as 80 cm s⁻¹ was calculated. Similarly, high values of the rate constant were obtained only using nanodes (microelectrodes of nm dimensions).¹⁰² This fact proves that ubiquinone molecules in the monolayer film behave as nanodes.

The mediated electroreduction of Ru(NH₃)₆³⁺ and electron tunnelling through ubiquinone were ruled out and a plausible mechanism, where loose conformation of isoprenoid chain in ubiquinone created a channel in LB film, that allows for a direct approach of Ru(NH₃)₆³⁺ ions to the electrode surface, was suggested. An additional confirmation of this hypothesis was found in the dependence of ubiquinone electroactivity on the cation size (Fig. 14). Obviously, the electroactivity of ubiquinone is severely hindered, when only a sufficiently large cation (tetra-butylammonium) is available in solution.

The kinetics (rate constant 80 s⁻¹)¹⁰⁰ has been obtained from CV according to the Laviron theory¹⁰³ and modified theory of Daifuku *et al.*⁸⁶ Compound **22** was also transferred onto a Au electrode by the LB technique¹⁰⁴ and the film exhibited a reversible two electron surface reaction in 0.1 M NaOH. The kinetics were slower at the lower pH. It is noteworthy that the electroactivity of the monolayer is complete and the CV response is symmetrical.

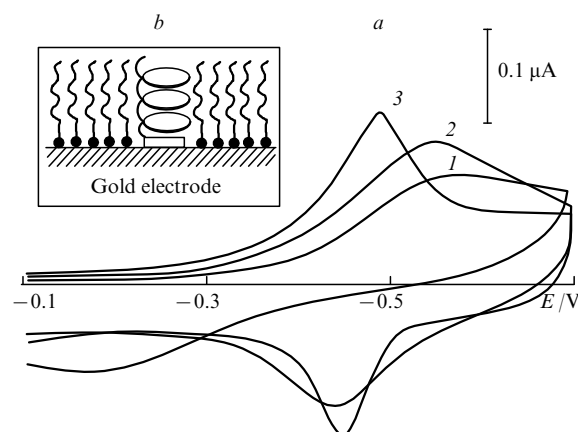
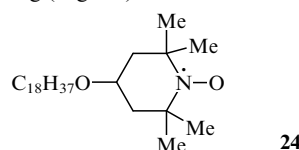


Figure 14. CV of ubiquinone **22** immobilised (1.5 mol.%) in a monolayer of C₁₈H₃₇SH/C₁₈H₃₇OH on a gold surface (a) and schematic representation of monolayer (b).¹⁰¹ Potentials *vs.* SCE: (1) 0.4 M Bu₄NOH; (2) 0.4 M Bu₄NOH + 0.02 M K₂SO₄; (3) 0.4 M Bu₄NOH + 1 M K₂SO₄, $\nu = 50$ mV s⁻¹.

The study of monolayers with the amphiphilic nitroxyl radical **24**¹⁰⁵ has shown that both pure monolayers and monolayers highly diluted with icosanoic acid show a defined 'break-in' effect, where electroactivity increases to a maximum upon voltammetric cycling (Fig. 15).



Both monolayers show responses with peak current proportional to scan rate, but high peak separations (100 mV) and peak half widths greater than theoretically expected 90 mV. Monolayers of pure material show a less symmetric CV response and two peaks were observed for oxidation, which can be explained by interaction between electroactive sites. More difficult to explain is the dependence of the 'break-in' effect on supporting electrolyte concentration, namely that at higher electrolyte concentration more cycles were necessary to achieve the maximum wave. It was suggested¹⁰⁵ that this phenomenon is similar to the 'salting-out effect' at the interface of aqueous solution and a hydrophobic monolayer.

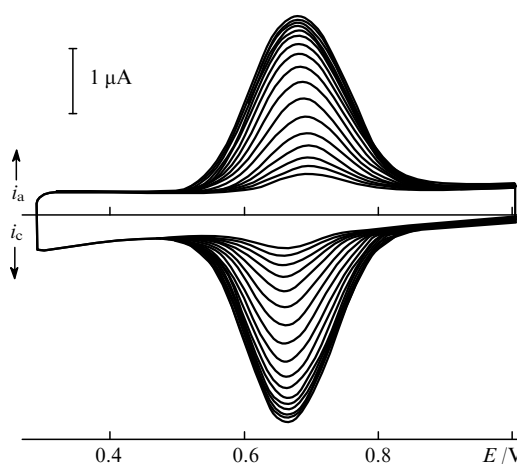
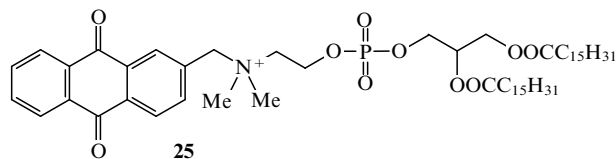


Figure 15. CV of a monolayer film of mixture of **24** and icosanoic acid (1 : 2), 0.18 M H₂SO₄, $\nu = 100$ mV s⁻¹, potentials *vs.* SCE.¹⁰⁵

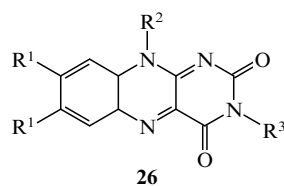
Using a phospholipid with attached electroactive anthraquinone moieties **25** authors¹⁰⁶ studied the influence of deposition surface pressure, composition of LB layer, nature of supporting electrolyte and the number of layers.



When the monolayers were transferred as a liquid expanded phase a surface wave response was observed and the best shape was observed in the 1:1 mixture with dipalmitoylphosphatidylcholine (Fig. 16a). Electroactivity of the films was complete, but the peak half width was considerably higher (80 and 120 mV) than predicted for a two electron surface wave (45 mV). Film transfer in the solid condensed state results in incomplete reoxidation and a postwave after the main reduction peak. This effect was increased in KCl electrolyte (Fig. 16b). Only the inner monolayer was electroactive in Y-type three layer films consisting of either the same molecules or two nonelectroactive layers. This signifies that the two outer monolayers inhibited charge transfer to the inner monolayer (Fig. 16c). All these observations were consistent with hindered ion transport through LB films. The SA films of the same compound **25**¹⁰⁷ showed low peak separation in KCl solution. However, peak splitting appeared upon potential cycling.

Flavin is one of the typical prosthetic groups of electron transfer proteins. Ueyama and co-workers¹⁰⁸ studied a flavin (**26a**) LB monolayer on a gold electrode.

A surfactant molecule was deposited in the solid condensed state with mean molecular area 0.47 nm². Peak half widths in voltammograms were much larger than the theoretical value and

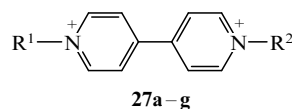


26a: R¹ = Me, R² = R³ = C₉H₁₉;

26b: R¹ = CH₂SCH₂CO₂H, R² = R³ = C₉H₁₉.

the shape of the response was of a diffusion-controlled type. The dependence on scan rate of peak current was also closer to diffusion controlled behaviour than to surface reaction. Thus a first-order rate constant according to the surface reaction model (about 1.5 s⁻¹)⁸⁶ does not have much validity. In addition electroactivity of the film was not complete even at slow scan rates. Another amphiphilic flavin molecule **26b**¹⁰⁹ showed a better surface wave response for a monolayer film possibly due to higher mean molecular area and consequently more facile ion diffusion.

Bard and co-workers¹¹⁰ studied amphiphilic viologen **27b** in the form of LB and SA monolayers.



27a: R¹ = Et, R² = CH₂CH₂CON(C₁₈H₃₇)₂;

27b: R¹ = Me, R² = C₁₆H₃₃;

27c: R¹ = Et, R² = C₅H₁₀OPhNNPhOC₁₂H₂₅;

27d: R¹ = Me, R² = C₂₂H₄₅;

27e: R¹ = R² = C₁₆H₃₃;

27f: R¹ = R² = C₁₈H₃₇;

27g: R¹ = R² = C₂₂H₄₅.

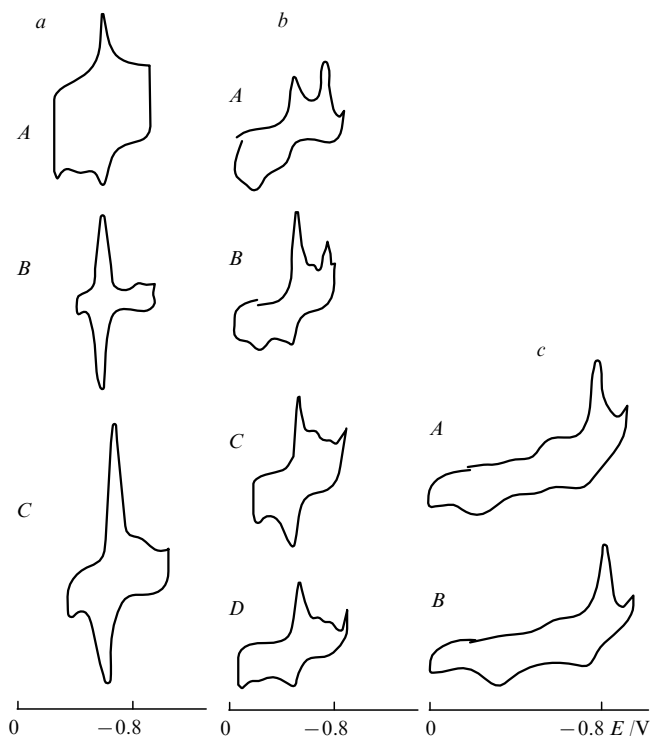


Figure 16. CVs of monolayer of **25**.¹⁰⁶

Potentials vs. SSCE; (a) in 0.2 M NaClO₄, 50 mV s⁻¹, transferred at 25 mN m⁻¹, molar contents of **25** in monolayer 0.1 (A), 0.5 (B), 1.0 (C); (b) in 0.2 M KCl, $v = 200$ mV s⁻¹, transferred at 40 mN m⁻¹ (A), 31 mN m⁻¹ (B), 25 mN m⁻¹ (C), 15 mN m⁻¹ (D); (c) in 0.2 M KCl, 200 mV s⁻¹, transferred at 25 mN m⁻¹: (A) Y type 3 layer, (B) monolayer of **25**, covered with 2 layers of nonelectroactive surfactant.

The LB monolayers with mean molecular area 0.40 nm² were completely electroactive. Two definitive reduction and oxidation peaks were observed (Fig. 17), which is in agreement with the theoretical model in the case of sufficiently negative interaction energy.³⁰ In contrast, a SA monolayer, which was not as closely packed as the LB monolayer and had more random orientation of molecules, showed only a single peak. In simple chemical terms strong pairing of the dication with the radical-cation results in the mixed valence state exhibiting a different reduction potential compared to the parent dication state. A similar explanation can apply to prepeak observations in LB films of derivative **1c**,²² whose parent compound BEDT–TTF is well known for a strong intermolecular interactions in a mixed valence state, in **2b** LB films,²⁹ and with oligoimides **13**.^{63, 64}

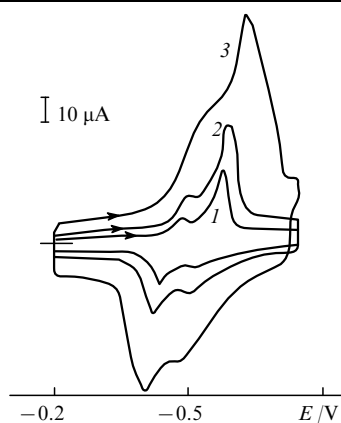


Figure 17. CVs of **27b** monolayer LB films on ITO electrode in 0.2 M NaClO₄.¹¹⁰

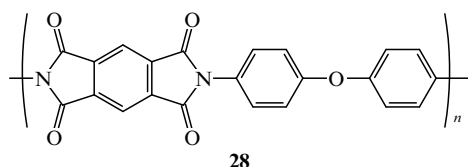
Potentials vs. SSCE, scan rate (mV s⁻¹): 100 (1), 200 (2), 500 (3).

The same group studied amphiphilic viologen **27d**, which forms much denser films (molecular area about 0.2 nm²) and demonstrates more stable electrochemical properties.¹¹¹ Better developed splitting of the first reduction peak was observed for these films.¹¹⁰ However, when viologen was sufficiently diluted with icosanoic acid, the monolayer showed only single peaks in CV indicating the absence of the interaction between viologen sites.

For comparison, LB monolayers formed by symmetrical viologen amphiphiles **27e–g** were studied.¹¹² Only single redox peaks were observed. The films were loosely packed as was deduced from the higher molecular area, the contact angle measurements and electrochemical experiments with solution redox probes.¹¹² Thus, the loose structure and, consequently, smaller possibility for intermolecular interactions can account for the single peak behaviour. The reduction potentials for the surface confined viologen in all LB films studied^{110–112} were more positive than for the viologen in solution. This was attributed to the stabilisation of the radical-cation form compared to the dication form in the LB films due to the more hydrophobic environment. The effect is probably similar to the one observed for SA monolayers of Fc substituted thiols on Au.¹¹³

The reduction peak splitting for asymmetrical viologen **27b** depends on the nature of electrolyte.¹¹⁴ The peak splitting was also observed in the response of SA monolayers. However, only CV of LB monolayers with bulky anions displayed double peaks.

Fujihiro and co-workers¹¹⁵ reported on LB films of polyimides **28**. The films were obtained by the thermal chemical reaction of an LB film of the precursor polymer.



A facile electrochemical reaction involving two reduction steps was observed. The electroactivity of the film was proportional to the number of layers (at least up to 30 layers). Unfortunately, the electroactivity decreased upon potential cycling.

The electrochemical technique has been used for detecting methylene green (a water soluble dye) in the LB films, transferred from a mixed monolayer of a phospholipid.¹¹⁶

The study of photosensitised electron injection in xanthene dyes, immobilised into LB films of Cd icosanoate, has been reported.¹¹⁷ The dependencies of current on potential without and with illumination by light of different wavelength (photo-current spectroscopy) were investigated. Similar studies have been done for LB films of halobacterial violet,¹¹⁸ where the effective photocurrent depended on the pH and potential. It was suggested that this phenomenon could be used in the fabrication of a luminance sensor. The photochemistry of the xanthene dyes, immobilised into LB films and deposited onto anthracene crystal, was also investigated.¹¹⁹

The electrochemical properties of LB films of bacterial photosynthetic membranes were also reported.¹²⁰

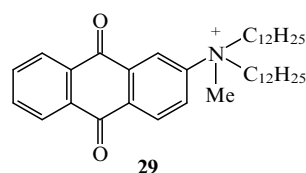
LB films discussed in this chapter are interesting objects for the study of surface electrochemical reactions, influence of the conditions of LB film transfer on the electrochemical properties of the coated electrodes and modelling of the properties of biological membranes.

VI. Heterolayers

It was suggested^{121–123} that the positively charged viologen amphiphile **27c** forms bilayers with negatively charged poly(1-sulfatoethylene) and other polyelectrolytes. The electroactivity of the films increased with the number of layers, but was not proportional to this number, which means that in a multilayer assembly electrochemistry became more difficult.¹²¹ Peak current

became proportional to the square root of the scan rate for films of more than five bilayers which indicates that electrochemistry is limited by diffusion of ions through the LB film.^{121, 122} Reduction in the first cycle needed higher overpotential and a stable voltammogram was established after a few scans.¹²¹ Quartz crystal microbalance studies indicate ion transport and morphological changes in the films during the electrochemical process.¹²¹ It was also found that the reduction potential for the viologen **27c** is strongly affected by the structure of polyion. The smaller the molecular area of the complex at low surface pressure the lower the reduction potential.¹²² Thus, more compact films required a higher overpotential. For LB films formed with polyacrylic acid¹²³ the reduction potential was found to depend on the pH of the subphase during LB transfer and the pH of the electrolyte in the CV experiment.

Fujihiro and Araki studied a different assembly of LB layer comprised of anthraquinone **29**, viologen **27a** and ferrocene **18a**.^{124, 125}



Multilayers were constructed from an inactive layer of icosanoic acid and electroactive mixed layers (electroactive surfactant + icosanoic acid). All types of anthraquinone-containing multilayer assemblies were electroactive and the proposed mediator for electron transfer through inactive icosanoic acid layers were either electroactive surfactant molecules penetrating through these layers (which seems quite impossible) or traces of oxygen.¹²⁵ The authors estimated a first-order surface reaction rate constant, from peak separations, decreasing with increasing number of inactive layer of icosanoic acid. It seems that electroactivity, as shown by CV,¹²⁵ is at least an order of magnitude smaller relative to the amount of deposited materials. In some cases CV response was not higher than the background current.¹²⁵

On reduction of viologen to its neutral state a gradual decrease of peak current was observed until the redox response completely disappeared. This indicates that the viologen surfactant forms a compact hydrophobic structure in the neutral state, so that reoxidation is blocked owing to hindered diffusion of counterions. For the Fc containing multilayer assembly **18a** no peaks of Fc oxidation were seen. A possible explanation of this fact may be found from a study of a viologen multilayer assembly as Fc containing multilayers are neutral. Facci¹² observed blocking of electron transfer from a Fc monolayer divided by one layer of Cd stearate spacer. A more complicated structure **29**/icosanoic acid/**27a** was then constructed.¹²⁵ This assembly showed anthraquinone reduction and a first viologen reduction. However, if the potential was held at –1.5 V to reduce the viologen layer to the neutral state, the compact viologen layer hindered the reduction of the inner anthraquinone layer. Electroactivity could be recovered at least partially by reoxidation of the film for 5 min at 0 V.¹²⁵

Ueyama and co-workers¹⁰⁸ studied heterojunction multilayers constructed from amphiphilic flavin **26a** and Ru porphyrin **17**. The theoretical model previously developed for multilayers of one compound¹²⁶ was extended to the heterojunction of two monolayers.¹⁰⁸ CVs for flavin, Ru porphyrin and a heterojunction between them are shown in Fig. 18. The shape of the CVs show general agreement with simulated ones. The common features are as follows:

1. Peak potential in the first sweep is similar to Ru porphyrin and no peaks are observed near the flavin peak potential.
2. Anodic peak current in the first sweep is higher than in the subsequent one and charge consumed under the peak corresponds to the sum of the oxidation for flavin and porphyrin.
3. Charge in the second sweep corresponds only to porphyrin oxidation.

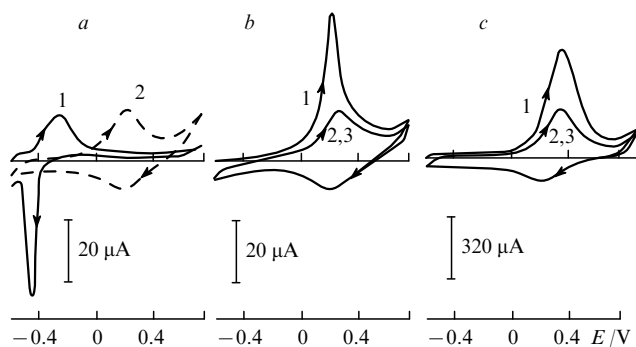
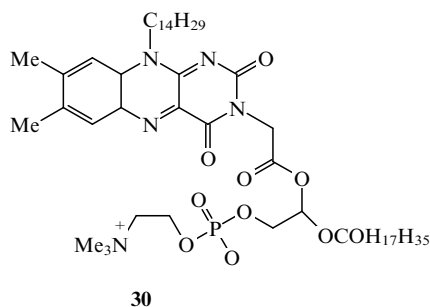


Figure 18. CVs for monolayers of **17**, **26a** (a) and Z heterolayer (3 layers of **17** + 1 layer of **26a**) (b, c) electrodes in 0.1 M NaClO₄.¹⁰⁸ Potentials vs. Ag/AgCl; (a) $v = 0.05 \text{ V s}^{-1}$, solid line — **26a**, dashed line — **17**; (b) $v = 0.05 \text{ V s}^{-1}$; (c) $v = 0.8 \text{ V s}^{-1}$; indicated numbers of cycle.

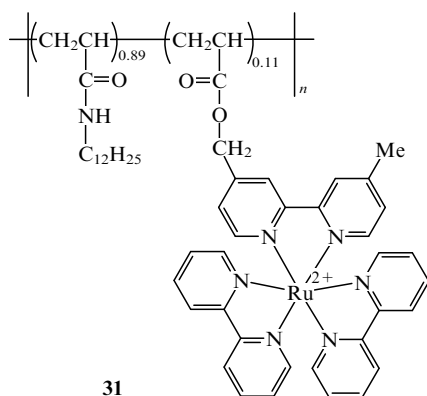
Theoretically this corresponds to the case where electron transfer in one direction from reduced flavin to oxidised porphyrin is much faster than in the opposite direction. Using simulated and experimental CV the electron transfer diffusion coefficient was estimated as $1.9 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ for the favoured direction and $1.5 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$ for the opposite direction. Pseudo-first-order rate constants were estimated as 64 s^{-1} and $\leq 0.25 \text{ s}^{-1}$, respectively.

A bilayer of flavolipid **30** — cytochrome *c* showed similar behaviour.¹²⁷



In this case electron transfer was much faster from flavolipid to cytochrome.

The electrochemical response of the LB heterolayer, consisting of 3 layers of Ru complex copolymer **31**⁹⁴ with an oxidation potential of 1 V vs. SCE and 2 layers of Fc co-polymer **20b** with an oxidation potential of 0.35 V vs. SCE, is shown in Fig. 19.



In the first cycle, no oxidation current was observed at the Fc redox potential of 0.35 V, because Fc could only be oxidised through the reduced inner layer of Ru complex co-polymer **31**. Fc oxidation appears as a sharp catalytic current at the potential, where Ru(II) is oxidised. Upon repeated cycling, only the redox

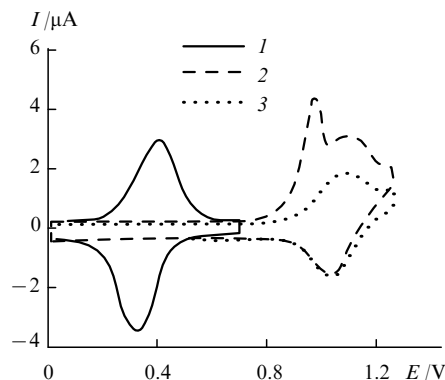
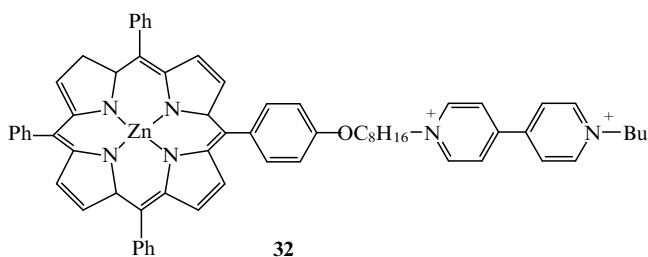


Figure 19. CVs of the LB films of co-polymers on ITO electrode. Potentials vs. SCE, in 0.1 M NaClO₄, $v = 10 \text{ mV s}^{-1}$; (1) 3 layers of copolymer **20b**; (2) 3 layers of copolymer **20b** + 2 layers of copolymer **31**, first cycle; (3) the same, second cycle.⁹⁴

peaks for the Ru(II)/Ru(III) couple are observed as ferricinium can not be reduced, and the charge is trapped in the outer Fc polymer layers.

It has been suggested earlier¹²⁸ that vectorial electron transfer might be obtained, if redox moieties can be placed in a potential gradient along the polymer chain. This idea has partly been substantiated^{129,130} using two differently substituted *p*-benzoquinone species or *p*-benzoquinone and bipyridyl species immobilised on Au surface by the SA technique. Recently, we suggested a novel approach to this idea by LB technique⁹¹ using multiredox centre molecules **18f–h**. For this, redox molecules **18f–h** were incorporated into an LB array of fatty acid. Direct confirmations of uni-directional electron transfer were not obtained, but electrochemical response of LB arrays differed considerably from that of the randomly oriented cast films suggesting a certain degree of organisation in the LB films. Fig. 20 shows the difference in the CV response for the LB and cast films of the compound **18g**. It is notable that only one peak appears in the LB film of **18g** mixed with fatty acid. An orientation of **18g** with the Fc moiety closer to the electrode surface than the TTF group seems likely.⁹¹ Compound **18f** contains two equivalent Fc redox centres. The experimental observation of the two peaks in CV for the LB films of **18f** mixed with fatty acids led to the conclusion of the ordering of **18f** molecules in an LB array, where two Fc moieties are at a different distance from the electrode surface, and consequently, in a different environment.⁹¹ The peak splitting due to intermolecular interaction³⁰ was ruled out as the dilution of the LB films with fatty acid did not lead to the disappearance of double peaks.

Recently, LB films of amphiphilic diad molecule **32** have been studied.¹³¹



Such porphyrin diads are of interest for modelling of an electron transfer in biological systems. It was shown¹³¹ that a magnetic field in any direction increases the anodic photocurrent at 0 V vs. Ag/AgCl and that electron transfer from the porphyrin onto the electrode is mediated by viologen.

Different bilayer assemblies, containing amphiphile **18d** were studied to understand the possibility of long-range electron transfer.¹² In contrast to the results of Fujihira *et al.*^{124,125} less defective

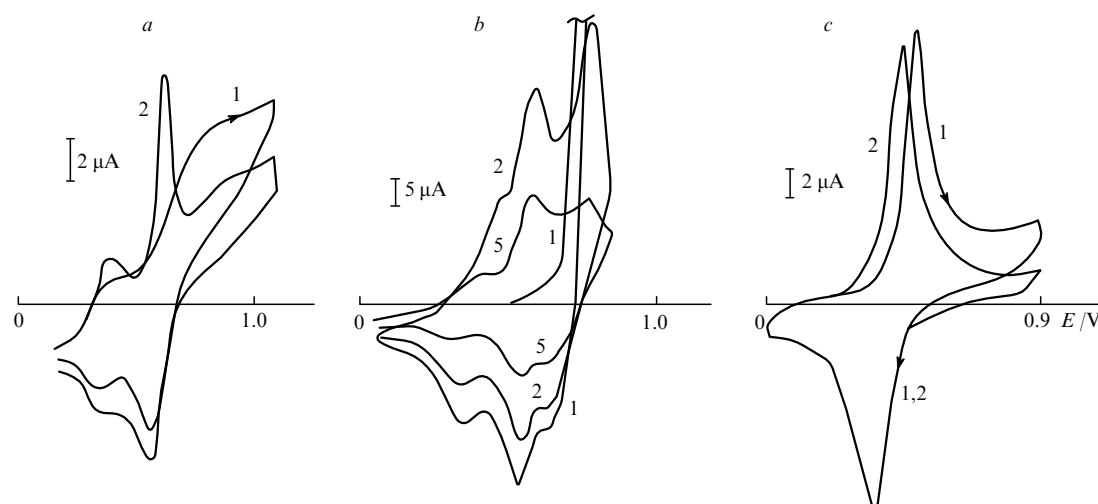


Figure 20. CVs of LB films of **18g** in 0.1 M HClO₄, $v = 200 \text{ mV s}^{-1}$.⁹¹

Potentials vs. Ag/AgCl; (a) cast film, (b) LB film of pure **18g**, (c) LB film of **18g** mixed with 20 mol.% of tricosanoic acid, cycle numbers indicated.

films of Cd stearate were employed in this work. When one monolayer of a spacer, cadmium stearate, was deposited between Au and the **18d** monolayer, electron transfer was completely blocked (a distance of about 2.5 nm from the electrode). For a bilayer of a mixture of **18d** and Cd stearate, where the electroactive head of the first layer was oriented away from the gold and adjacent to the electroactive head of the second layer, a CV response was observed, but electroactivity was not higher than 10% and an additional reduction peak appeared. If the second layer in such a bilayer consists only of cadmium stearate electroactivity increased to 60%, which signifies that only the inner layer is electroactive. However, in this case both anodic and cathodic peaks were split. Broadening and splitting of the peaks was explained accordingly.³⁰ Other possible explanations include different Fc environments or geometric arrangements.

In more recent reports^{132, 133} the electron transfer at smaller distances was probed. A SA layer of alkanethiol on gold was employed as a spacer to determine the distance for the long range electron transfer. The advantage is that SA monolayers of alkanethiols on gold have smaller defect concentrations than LB films. The electrochemistry of SA monolayer with attached electroactive groups was investigated in several reports.^{134, 135} However, in this case electron transfer could occur through a bond in the alkyl chain. In the case when the LB layer of the amphiphile **18e**¹³³ was deposited on the top of the SA spacer, only through-space electron tunnelling is possible. Preliminary studies with a monolayer of decanethiol¹³² have shown that electrochemistry of **18e** was affected by the composition of the subphase, which was also used as the electrolyte for voltammetry, and the conditions of the film transfer. Two redox couples (0.22 and 0.4 V vs. SCE) were observed for pure **18e** on the 0.1 M NaClO₄ subphase. The diffusion of **18e** to defect sites in the SA monolayer was ruled out as thiol monolayer completely blocked electrochemical reaction of hexacyanoferrate(III) in solution. It was postulated that because of the mismatch between the molecular areas of the head and tail groups in **18e** a high degree of molecular packing was not possible¹³² and the first redox couple is associated with the defects in the LB film, where free counterion transport is allowed. The redox couple at 0.4 V is associated with hindered counterion transport to the Fc sites in a more hydrophobic environment. This corresponds to the report of Creager and co-workers¹¹³ on the increase of the Fc redox potential with increasing hydrophobicity of the environment. White's theoretical treatment¹³⁶ can also explain these results. In the case of **18e** diluted by fatty acid no electrochemical response of Fc was seen. The data of the surface pressure–molecular area isotherm and ellipsometry support the idea that the very densely packed bilayer

structure with alkyl chains of fatty acid filling in the space in the tail groups of **18e** is formed. Such a compact hydrophobic environment completely blocks counterion permeation to the Fc redox sites and consequently electrochemical reaction is inhibited. On the other hand it was shown that **18e** does not form miscible layers on the HClO₄ subphase.¹³² These films are not densely packed and electrochemical reaction could be observed. However, even on the HClO₄ subphase the electroactivity was not complete and it was necessary to transfer films in the expanded state (with molecular area of 3 nm² or even higher, using the horizontal transfer technique). Also if a floating layer was left on the subphase surface for more than 20 min ill-defined CVs were observed. So to ensure a sufficient number of defects in the film for facile counterion transport the floating layer was left on the subphase surface for not more than 5 min. The electron transfer kinetics for SA films of thiols with 10, 12, 14, 15 and 18 carbons were determined according to the Laviron theory.¹⁰³ The dependence of first-order rate constant on the length of alkyl chain in thiol was linear with a decay constant of -0.99 per methylene group. The comparison of these data¹³² with those obtained for the Fc terminated thiols showed that at a distance of 1.4 nm from the electrode surface, electron transfer was almost two orders of magnitude slower. The largest distance was 2 nm (thiol C₁₈H₃₇SH)¹³³ and it is possible that a complete blocking of the electrochemical reaction was not achieved (compared with the previous results,¹² where this distance was about 2.5 nm).

Using a monolayer of Fc amphiphile **18b** on an interdigitated microarray electrode covered with a monolayer of SA film lateral diffusion in a monolayer has been studied¹³⁷ (the transfer on bare electrode was not satisfactory). If all arrays in the interdigitated electrode are connected together the usual surface wave response (Fig. 21 a), with some diffusion tailing due to electroactive material diffusing between the arrays were obtained. Generator–collector voltammograms, shown in the same Fig. 21 b, were obtained when one set of microelectrodes is made oxidising and another is made reducing with respect to the Fc formal potential. Using appropriate theory and steady state collector voltammogram the authors¹³⁷ calculated the lateral diffusion coefficient to be around $(2-4) \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ depending on the surface pressure used for monolayer deposition. It should be mentioned that the diffusion coefficient decreased when the monolayer became more densely packed. These diffusion coefficients were an order of magnitude smaller than for Langmuir monolayers on a water surface. It was explained as a change of fluidity of Fc molecules and it seems it is only possible because the LB films were studied in a liquid expanded state. In the following work¹³⁸ the behaviour of these films was studied in more detail. Since the electrochemical

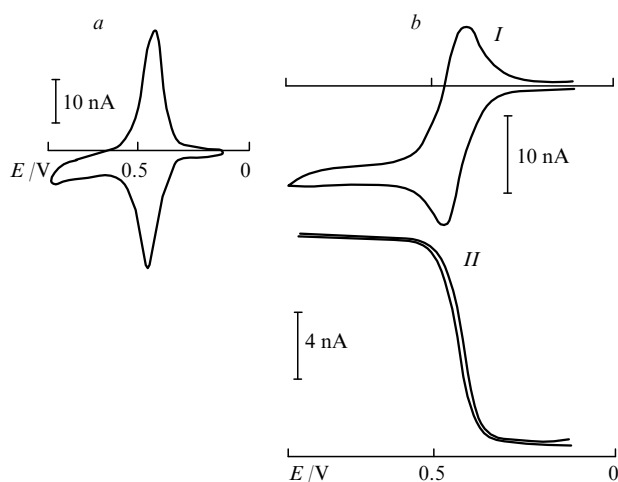


Figure 21. CV (a) and generator–collector voltammograms of the same system (b) of **18a** on an interdigitated microelectrode array.¹³⁷ (a) Potentials vs. SCE, with both sets of electrodes driven at the common working electrode potential, 1 M aqueous LiClO₄, $\nu = 20 \text{ mV s}^{-1}$; (b) generator electrode scanned from 0 to 0.9 V and the collector electrode held at +0.1 V, $\nu = 20 \text{ mV s}^{-1}$, (I) generator current–voltage curve, (II) collector current recorded at +0.1 V and plotted vs. the potential of generator electrode.

properties were studied using the usual planar electrodes, it implied that electrons are tunnelling over a distance of about 5 nm. This seems impossible in view of the results previously reported.¹² Therefore, it was proposed¹³⁸ that electron transfer occurs by lateral diffusion to defect sites in the LB film. However, it is not proven since the voltammetric response possesses the shape of the surface wave response.¹³⁸ The voltammetric response seems to be very sensitive to the time the monolayer was left on the subphase surface before compression, the compression rate, the surface pressure for the film transfer and the time monolayer was left after compression. For instance, the films transferred at the high pressure (where the staggering of molecules is supposed) postulated the shoulder on the oxidation peak.

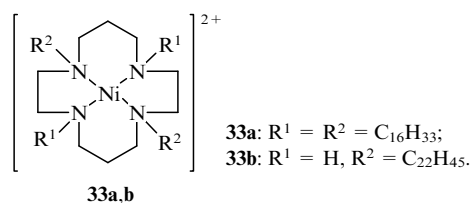
The decrease of the electroactivity in the following cycles was explained by the gradual embedding of Fc head groups in the hydrophobic part of monolayer according to the theoretical treatment of White and co-workers.¹³⁶ The electroactive coverage also decreased with the increase of the compression rate and the increase of the time the monolayer was left on the subphase surface before compression. This was ascribed to the two-dimensional reorganisation in the monolayer leading to the burying of Fc head groups in the hydrophobic part of the monolayer. This fact was observed by the AFM (transition from a liquid expanded to a liquid condensed state).¹³⁸

The deposition of ubiquinone **22** on a hydrophobic Au electrode covered with SA monolayer results in only partial electroactivity of ubiquinone. The electroactivity was assigned to the molecules of **22** residing on the defect sites of the SA monolayer.¹⁰⁴ This observation corresponds to the report,¹² where electrochemical reaction was not observed for Fc amphiphile **18d**, when monolayer was deposited onto the top of a passivating monolayer of Cd stearate. Ubiquinone incorporated in a phospholipid bilayer¹⁰⁴ LB film showed distinctive features of diffusion controlled behaviour. This was explained by the diffusion of ubiquinone through the lipid bilayer to the defect sites in the SA monolayer.

VII. Applications

Some of the electroactive LB films showed electrocatalytic properties. A Ni cyclam **33a** LB monolayer on a glassy carbon electrode

was active in the electroreduction of CO₂ in aqueous electrolyte at pH 4.5.¹³⁹

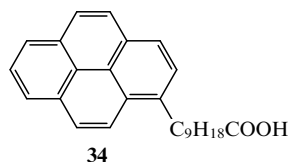


Later,¹⁴⁰ these results were found to be irreproducible and LB films of monosubstituted Ni cyclam **33b** have been prepared. The 1–3 layer films exhibited complete electroactivity, surface wave response and electrocatalytic reduction of CO₂.

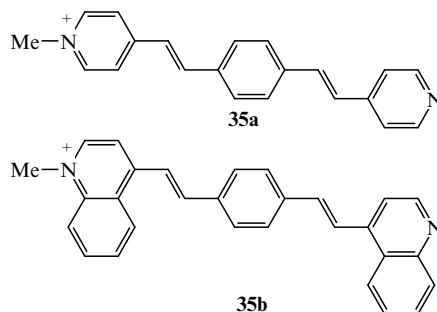
The films containing complexes **21a,b**⁹⁵ and bis-Fc¹⁴¹ catalysed some electrochemical reactions. A monolayer containing a Ru complex **21c** electrocatalysed the oxidation of oxalate anions and generated chemiluminescence.⁹⁸

The LB technique was also used for the formation of thin electrocatalytic electrodes loaded with Pt particles.¹⁴² These electrodes had similar activity to smooth Pt electrodes but with a much lower Pt loading level. Catalytic activity in such thin electrodes (~10 nm) cannot be limited by the mass transfer through the film. The electrodes were obtained by LB deposition of the amphiphilic compounds from a H₂PtCl₆ containing sub-phase with subsequent electrochemical reduction of the incorporated PtCl₆²⁻ anion to Pt metal.

Different approaches for the fabrication of electrochemical diodes have already been discussed above. Using a biomimetic approach of electron transfer in biological systems to model the molecular electronic devices Ueyama and co-workers^{108,109,126} fabricated multilayer LB assemblies with uni-directional electron transfer. This device can be considered as a molecular photodiode. Similar behaviour is observed in LB films of flavin with cytochrome *c* in solution,¹⁰⁹ LB heterolayers of flavolipid and cytochrome *c*,¹²⁷ Fc- and Ru-complex co-polymers,⁹⁴ and pyrene **34** and Fc **18a**.¹⁴³



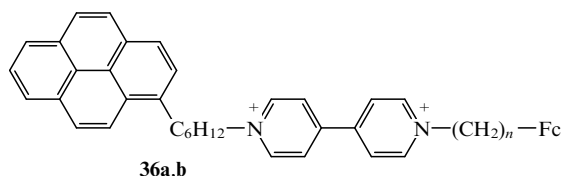
Recently^{144,145} LB films of conjugated molecules **35** were used for rectified electron transfer through a LB monolayer to solution redox species.



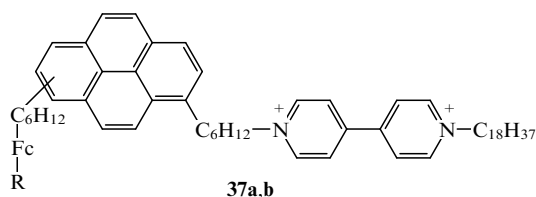
The monolayer of **35a** demonstrated a CV response with high peak separation. This might indicate either slow electrochemical kinetics or a diffusion controlled electrochemical reaction. The electrochemical response of [Fe(CN)₆]³⁻ in solution was blocked by a monolayer of compounds **35**. It should be emphasised that it is not easy to fabricate a passivating monolayer by the LB technique. For instance, Bilewicz and Majda⁸⁷ used a monolayer of a mixture of C₁₈H₃₇SH and C₁₈H₃₇OH to achieve good passivating properties on the surface of a gold electrode. This

involves SA of thiol by covalent bonds and decreases, thus, the defect concentration in the monolayer. Therefore the passivating properties of the last monolayer were similar to those of monolayers of SA thiols. The hexacyanoferrate(II) reduction was mediated by the monolayer (an increased peak in the CV response) and the re-oxidation was blocked, which was also confirmed by chronocoulometry. It was suggested^{144, 145} that these amphiphiles with long conjugation might serve as a 'molecular wire'. However, it remains unclear whether the electron transfer occurs 'through space' or 'through conjugated bonds' in the LB film. Mixed monolayers of the compounds **35** displayed an electrochemical response characteristic of the ultramicroelectrode array.¹⁴⁵

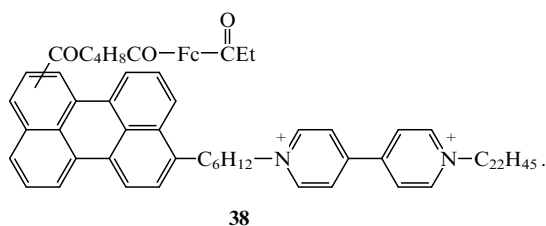
Electrochemical photodiodes have been fabricated by a LB technique.¹⁴⁶ Using **29** as an electron acceptor (A), **34** as a sensitizer (S) and **18a** as an electron donor (D) and combining the monolayers into the multilayers as A–S–D or D–S–A, the vectorial current was registered.¹³⁵ The direction of the observed photocurrent was in good agreement with the energy profile of the film components. Subsequent studies have concentrated on the fabrication of similar devices using a monolayer of a molecule containing all components (intra-molecular photodiode).^{146–151} Several triad molecules **36–38** were synthesised:



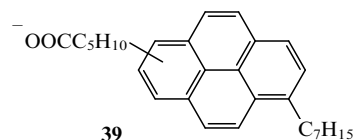
$n = 11$ (a), 16 (b).



R = H (a), Pr (b).

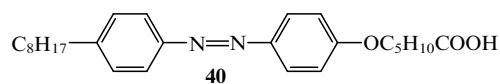


These triad molecules allow the creation of the structure A–S–D as only the viologen (A unit) is hydrophilic within the triad. Due to the two alkyl chains the compound **37b** allows the fabrication of a film with the opposite orientation D–S–A¹⁵¹ on a hydrophilic support. The direction of the observed photocurrent in all cases considered was in good agreement with the energy diagram of the D, S and A moieties in the film. The highest photoelectric conversion efficiency was registered for photodiodes based on compound **37a**.^{148–150} Also, in order to model the transfer of light energy in photosynthesis, monolayer films of a mixture of compounds **38** and **39** were fabricated.¹⁴⁹



In this case compound **39** worked as a light harvesting antenna and the energy transfer from the pyrene moiety of **39** occurred onto the perylene moiety of **38**. The photocurrent was generated after multistep electron transfer through the monolayer.

Japanese group^{152–155} proposed an interesting photoelectrochemical 'one-way' process based on the difference between the electrochemical reductions of *trans*- and *cis*-isomers of an azo-compound **40** in LB films.



The *cis*-isomer of surfactant azobenzene was much easier to reduce (difference in peak potentials about 400–600 mV depending on pH) than the *trans*-isomer (Fig. 22). However, oxidation of hydrazobenzene yielded only the *trans*-isomer of azobenzene. The *trans*-isomer can be transformed to *cis*-isomer by illumination. This 'one-way' process can be used for high-density information storage either by 'optical writing' (using laser beam) or 'electrochemical writing' (counter electrode probe positioned as in a scanning tunnelling microscope).^{152, 153} Information can be read spectroscopically as well. It has been shown later¹⁵⁶ that to further improve storage density the information can be written and read using linearly polarised UV light. Recently, this material has been deposited by the LB method on Au substrates modified with SA thiol monolayers.¹⁵⁷ The electron transfer distance was changed by varying the length of the thiol molecule and the orientation of molecule **40**. The orientation has been changed by choosing the thiol terminal group. When **40** was oriented with the octyl chain adjacent to the hydrophobic end of the alkyl thiol, the total length of 26 carbon atoms completely blocked electron transfer from the azobenzene moiety (Fig. 23). This corresponds to the results of reports.^{12, 133} In the case of the hydrophobic end of **40** adjacent to the hydrophilic end of HOCH₂CH₂SH the CV response was not observed. This was explained¹⁵⁷ by the change of the azobenzene electrochemistry from irreversible to reversible. The reduction potential of *cis*-azobenzene becomes more anodic than the re-oxidation potential of hydrazobenzene. Owing to this inversion of the redox potentials the reduction of *cis*-azobenzene cannot be observed. This hypothesis was supported by photoelectrochemical studies.¹⁵⁷

Another azo-derivative **41a** also demonstrated well resolved electrochemical properties. It may be used as a memory material through electrochemical means.¹⁵⁸

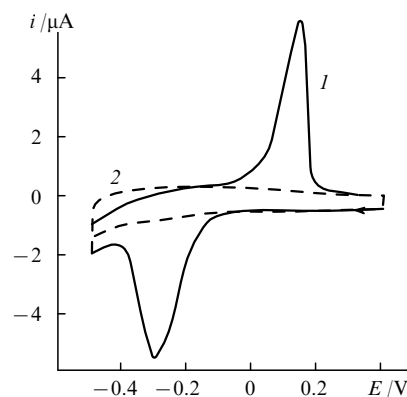


Figure 22. CV curves of monolayer film of compound **40** on an SnO₂ electrode, $v = 20 \text{ mV s}^{-1}$.¹⁵³ Potentials vs. Ag/AgCl; (1) *trans*, (2) *cis*.

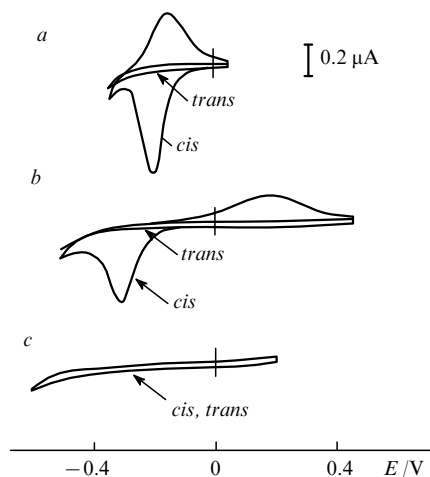
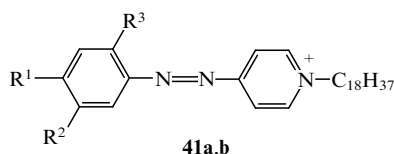


Figure 23. CVs of a monolayer film of **40** transferred onto an SA monolayer of thiol, 0.1 M aqueous NaClO_4 .¹⁵⁷

Potentials vs. Ag/AgCl , $\nu = 20 \text{ mV s}^{-1}$; (a) SA layer of ethanethiol (total length for electron transfer 10 carbon atoms); (b) SA layer of octanethiol (total length for electron transfer 16 carbon atoms); (c) SA layer of octadecanethiol (total length for electron transfer 26 carbon atoms).



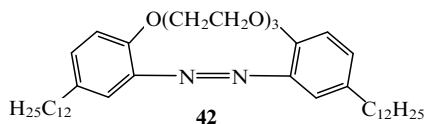
41a: $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{Me}$, $\text{R}^3 = \text{OH}$;

41b: $\text{R}^1 = \text{Me}_2\text{N}$, $\text{R}^2 = \text{R}^3 = \text{H}$.

Electrochemical properties of the LB films depended on the pH of the subphase and the following illumination of the film. The films transferred from the subphase at pH 3 exist in a *cis*-enol form and undergo the transformation into a *trans*-ketone form upon the illumination with 450 nm light. The last form exists in the LB film transferred from the subphase at pH 6.5. The same group¹⁵⁹ studied photoelectrochemical properties of the LB films of the other azo-derivative **41b**. The occurrence of the photocurrent was attributed to the tautomeric transformation of **41b** upon illumination. In CV this resulted in some change of the peak potentials and decrease of peak separation. It was suggested that these films may be useful for photogenerated information storage and for the fabrication of devices for photoelectric conversion.

A photoalarm based on a photocell using bacteriorhodopsin LB film deposited onto an ITO electrode has been constructed.¹⁶⁰

Amphiphilic azobenzenecrown derivatives¹⁶¹ were designed for the molecular recognition of cations. Monolayers of compound **42** were built up on Au or thin layer Hg electrodes.



While the CV response of the LB film on a gold electrode was unstable, the thin layer Hg electrode modified by the LB monolayer showed perfectly stable surface wave response. The peak separation was increased when the Li^+ cations in the electrolyte solution (peak separation 20 mV) were substituted by Na^+ or K^+ cations (80 and 400 mV respectively). This was attributed to molecular recognition in the LB monolayer due to complexation with the crown ether. Simultaneously the formal potential did not change significantly. We were the first to register electrochemical molecular recognition on the addition of alkali metal cations to films of polythiophene **12** deposited by the LB technique.[†] How-

ever, the electrochemical behaviour of these films did not show any advantages compared with the cast films of the same polymer.

LB films of polyaniline **8**, obtained as described above,^{54,55} were loaded with glucose oxidase during LB film transfer.¹⁶² These electrodes were used as an amperometric biosensor for glucose at the concentration level of 10^{-2} M .

The electrochemical analysis of trace quantities of water-insoluble electroactive compounds by on-trough voltammetry was described.¹⁶³ A specialised microtrough was constructed and water-insoluble compounds were transferred onto ITO or graphite electrodes by the horizontal technique at the low surface pressure. The deposited films were analysed by CV in the same trough. The minimisation of aggregation and the possibility to avoid water-soluble impurities were suggested as potential advantages over the casting of films onto the electrode surface. The application of this technique to the compound **21c** demonstrated linear dependence of CV peak area on the quantity of compound and the possibility of analysing this compound down to 2 pmol. The possibility of the analysis of other non-amphiphilic water insoluble redox active compounds was also demonstrated.

Thus, modified electrodes fabricated by the LB technique can be used in electrocatalysis and electroanalysis. Molecular electronic devices based on electrochemical and photoelectrochemical principles may be constructed.

VIII. Conclusions

LB films exhibit slow redox reactions if they are well ordered and densely packed. This results in a change of mechanism from the surface reaction model to diffusion controlled behaviour. In this case diffusion of the ions through LB film is the limiting process. Hindered voltammetry for multilayer assemblies is usually observed in this case and only the first inner monolayer may be electroactive. When LB films are not as well ordered or the molecule is large, which enables sufficient empty space between the hydrophobic chains, surface reaction response can be obtained. Due to the strong repulsive interaction in highly loaded films this response usually deviates from an ideal surface wave, leading to peak broadening, peak separation, peak doubling and additional peaks. Peak doubling, explained theoretically by sufficiently negative repulsive interaction, can be understood in simple chemical terms as dimerisation of molecules in different redox states in LB films. It is an especially useful explanation when the molecules are known to have strong interaction in crystals and solutions, leading to *p*-dimerisation and stack formation. Such kinds of molecules are often used for conducting charge-transfer complexes and radical-ion salts.

From the theoretical point of view the surface reaction model has been extended for LB monolayer, multilayer and heterolayer films and attempts to calculate *e*-transfer kinetic have been made. First-order *e*-transfer rate constant of 10^0 – 10^2 s^{-1} and pseudo-first-order rate constant for interlayer transfer of 10^2 s^{-1} have been obtained. An electron diffusion coefficient of 10^{-11} – $10^{-12} \text{ cm}^2 \text{ s}^{-1}$ and lateral diffusion coefficients in liquid expanded state of $10^{-8} \text{ cm}^2 \text{ s}^{-1}$ have been obtained. Vectorial electron transfer can be achieved in LB films with electron diffusion coefficients two orders of magnitude higher in the appropriate direction.

Electron transfer distance dependence has been probed using LB films electrochemistry. It can be concluded that electron tunnelling is possible over a distance of about 2–2.5 nm.

Electrochemical techniques can be used for producing electroconducting LB films of charge-transfer materials and LB films of conducting polymers. The electrochemical doping can be realised either on the trough during LB film transfer or as an electrochemical reaction after film deposition (including electropolymerisation in the LB films). Highly ordered conducting films can be

[†] L M Goldenberg, M Leclerc, M C.Petty, unpublished results.

obtained. Different counter-ions can be introduced into the films by this technique. However, further investigations are necessary to understand the dependence of the conductivity and other film properties on the structure of the counter-ion. The films with conductivity as high as 50 S cm^{-1} and a partially metallic temperature dependence have been obtained.

Improvement of film quality for electrochromic devices has been achieved. Interesting molecular electronic devices, especially based on a one-way photoelectrochemical process and vectorial electron transfer, can be fabricated using LB films. LB films have found an application in electrocatalysis.

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The use of palladium-catalysed cross-coupling for the synthesis of polymers incorporating vinylene and ethynylene groups

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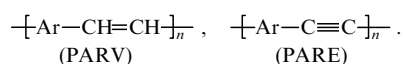
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Abstract. Methods for the synthesis of polyconjugated polyarylenevinylenes and polyaryleneethynylenes based on polycondensation catalysed by palladium complexes are reviewed. The bibliography includes 134 references.

I. Introduction

Synthesis of new π -conjugated polymers and investigation of their chemical and physical properties have attracted much attention in last decade.^{1–4} In this period polyacetylene,⁵ polydiacetylene⁶ and numerous polyarylenes incorporating aromatic carbo- and heterocycles^{7–10} have been obtained. Among these polymers, of special interest are the so-called polyarylenevinylenes (PARV) and polyaryleneethynylenes (PARE)



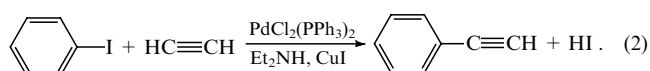
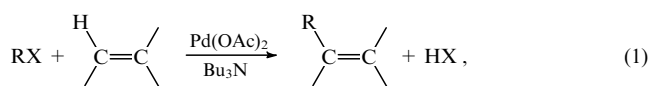
These polymers are distinguished by high electrical conductivity,^{1, 11, 12} relatively high non-linear third-order optical activity¹³ and electroluminescence.^{14, 15} Of current interest is the use of these polymers in light-emitting diodes.^{16–20}

Formerly, these polymers were prepared by the Wittig reaction²¹ and condensation according to McMurry.^{22, 23} However, due to the insolubility of polyarylenes, they are usually prepared *via* water-soluble intermediates or *via* products of the metathesis of corresponding cyclic compounds.^{24–26} Both methods include the stage of thermal elimination of low-molecular-weight products, which is not quantitative. As a result, the final products are contaminated with admixtures and this results in reduced electric activity of these materials.^{27, 28}

Hörhold *et al.*^{29, 30} used dehalogenation of *p*-xylylene systems to prepare soluble phenyl-substituted PARV. However, this approach has the same disadvantages as the aforementioned two-stage methods.^{24–26}

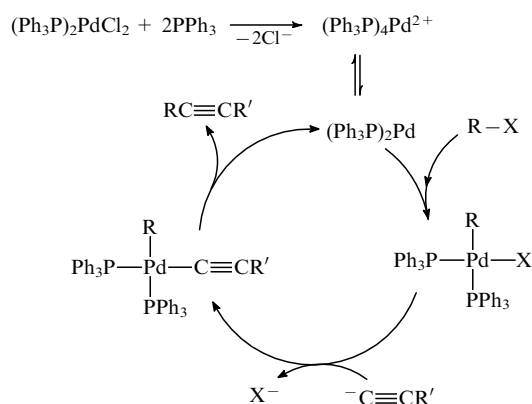
Syntheses of PARV or PARE type polymers are largely based on the studies by Heck *et al.*^{31–38} and Sonogashira *et al.*^{39–41}

devoted to the reactions of alkenes with aliphatic or aromatic iodides or bromides in the presence of Pd⁰ or Pd^{II} complexes. Usually, the reaction is performed either in the presence of 1 mol.%–5 mol.% of palladium salt or in the presence of Pd⁰ or Pd^{II} complexes with PPh₃ or other ligands, CuI as a promoter and a base (amine) that is needed to neutralise the hydrogen halide released and for the reduction of Pd^{II} to Pd⁰.



The Heck's reaction generally comprises two principal stages;³⁸ the first one is the formation of an organopalladium salt by oxidative addition, the second is the addition of the salt to alkene or acetylene with subsequent elimination of palladium hydride leading to the product of coupling. The selectivity of this process is determined by the reaction conditions and especially by the catalytic system. Thus when the Pd–AsR₃ system is used, two molecules of aryl halide are coupled; the yield of dimer is ~55%.⁴²

The mechanism of this process was studied in more detail using the formation of diarylacetylene as an example⁴³

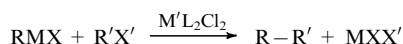


Reactions of organometallic compounds (Grignard reagents) with halogen-substituted organic compounds are also widely used for syntheses of PARV and PARE; these reactions are catalysed by Pd or Ni salts.^{44–50}

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M = Mg, Zn, SnBu₂; M' = Pd, Ni; L = PPh₃;

X, X' = Hal; R = Alk, R' = Alk, Ar, alkenyl, alkynyl.

The mechanism of these reactions is similar to that of reactions (1) and (2). On the first stage, the Grignard reagent and palladium-(or nickel)-phosphine complex form an organopalladium (organonickel) salt, which further yields coupling products in reactions with alkyl, aryl, alkenyl or alkynyl halides.

And finally, PARV and PARE can be prepared by reactions of aryl halides with alkynyl compounds in the presence of Pd complexes and phase-transfer catalysts.^{51–53}

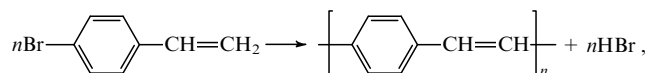
All aforementioned processes have substantial yields of by-products.⁵⁴ Hence these reactions of cross-coupling are far from ideal for polymer synthesis.⁹ Nevertheless, these reactions were used at different times for the preparation of PARV and PARE.

In this decade, one-stage direct reactions of aryl halides with vinyl- or ethynyl-containing compounds, which are catalysed by complexes of transition metals, primarily palladium complexes, are mainly used for synthesis of PARV and PARE.^{7–9}

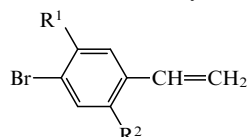
II. Synthesis of polyarylenevinylenes

The very first reports on the syntheses of PARV by Pd-catalysed cross-coupling^{55–57} considered various possibilities for their implementation, namely, homopolycondensation of 4-bromostyrene,⁵⁶ reaction of *p*-divinylarenes with dihaloarenes,⁵⁵ reaction of ethylene with dihaloarenes.⁵⁷

Homopolycondensation of 4-bromostyrene⁵⁶ according to the following scheme



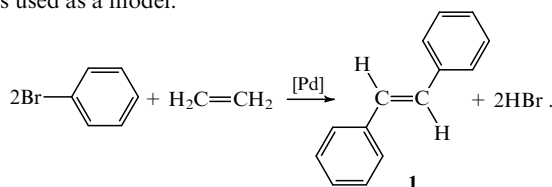
yields insoluble PARV, this predetermines its low molecular weight. It is possible in principle⁵⁷ to use in this reaction substituted 4-bromostyrenes of the general formula



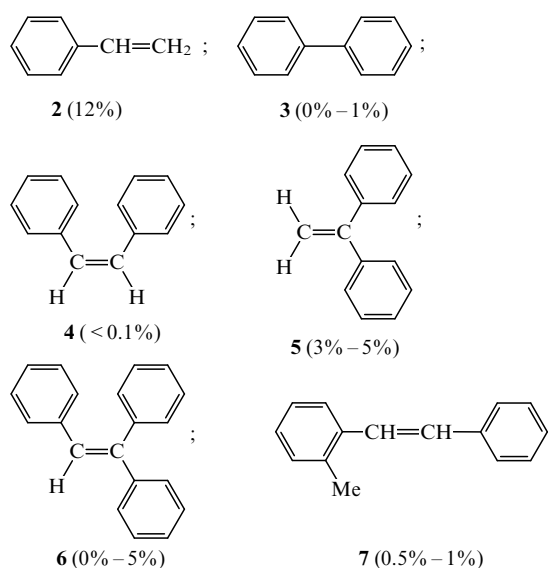
R¹ = H, R² = Me, Ph, CF₃; R¹ = R² = Me,

which provide a possibility of preparing polymers with improved solubility, however this synthetic procedure for PARV did not find much application.

A method based on the reaction of ethylene with dihaloarenes became more popular; this is due to the availability of the reactants. Heitz *et al.*^{42, 54, 57–60} have systematically studied this reaction. The reaction of ethylene with 2 mol of bromobenzene was used as a model.



This reaction was performed in the presence of a palladium acetate–tris(*o*-tolyl)phosphine–triethylamine catalytic system. It was found that, additionally to the target *trans*-stilbene **1** (75%–95% yield), compounds **2–7** were also formed:



The mechanism proposed by Heck³⁵ explains the formation of these compounds. Styrene (**2**) is formed in side reactions of bromobenzene, when excess of ethylene is used; biphenyl **3** is formed in the arylation of bromobenzene; *cis*-stilbene **4** appears as a result of conformational transformation in the transition complex; 1,1-diphenylethylene **5** is the product of α,β -addition of intermediate Pd–aryl complex with the alkene; triphenylethylene **6** is formed upon additional arylation of stilbene; *trans*-1-phenyl-2-*o*-tolylethylene **7** is a product of the reaction of ethylene or styrene with tris(*o*-tolyl)phosphine, which is used as a cocatalyst.⁵⁴

The side reactions of alkene with the cocatalyst and dehalogenation can result in lower molecular weight of the polymer, whereas formation of diaryls must not block the growth of macromolecules. The presence of triphenylethylene among the reaction products can result in the formation of cross-linked polymers.⁵⁴

The yield of the target *trans*-stilbene can be maximised and the role of side reactions substantially reduced if not suppressed by variation of such factors as the nature of halide and substituents in the haloarenes, composition and quantity of the catalyst, solvent, reaction temperature, pressure of ethylene.⁵⁴

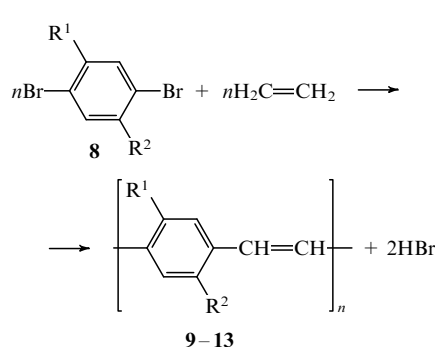
It was shown that (a) bromoarenes are most suitable for the purpose (chloroarenes have low reactivity, whereas iodoarenes sometimes have lower selectivity of the reaction compared to bromoarenes); (b) with bromoarenes, tris(*o*-tolyl)phosphine should be added as a cocatalyst, whereas it is not necessary for iodoarenes; (c) electron-acceptor substituents in haloarenes promote the reaction, while electron-donor ones do not; (d) a lower concentration of the catalyst, palladium acetate, brings about higher yield of the target compound and lower yield of side products (with the exception of 1,1-diphenylethylene); (e) the nature of solvent [acetonitrile, methanol, DMF, *N*-methylpyrrolidone (*N*-MP), *N*-methylcaprolactam, DMSO] affects the yield of the product (the highest yield of *trans*-stilbene was attained with the use of DMF); (f) an increase in the temperature accelerates the main reaction, while selectivity becomes lower (the temperature of 50–100 °C provides the maximum yield of *trans*-stilbene); (g) lower pressures of ethylene favour formation of stilbene and higher pressures, of styrene.

A systematic study of the reactions of non-substituted, mono-, and disubstituted *p*-dibromobenzenes **8** with ethylene, which proceed according to Scheme 1, was reported in Ref. 57.

Table 1. The weight-average molecular weights (M_w), softening temperature (T_s), decomposition temperature (T_d), and composition of PARV **9–13**.⁵⁷

PARV	R^1	R^2	M_w		T_s^c /°C	T_d /°C		Content of Br (%)	
			fraction I ^a	fraction II ^b		fraction I	fraction II	fraction I	fraction II
9	H	H	< 500	—	—	150	200	—	9.87
10	H	Me	1700	12 700	150	200	210	2.21	—
11	H	CF ₃	1000	3120	175	205	238	1.15	—
12	H	Ph	8000	—	155	210	290	0.71	—
13	Me	Me	900	2600	—	190	205	—	9.87

^aDetermined by GPC with polystyrene standard. ^bDetermined by GPC with poly(phenylene sulfide) standard. ^cDetermined using polarisation microscope at a heating rate of 10 deg min⁻¹.



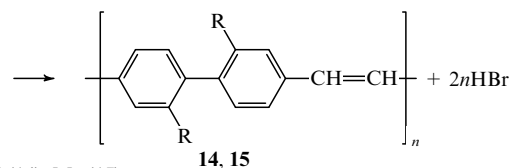
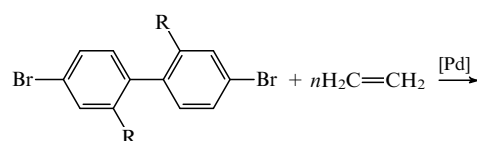
$R^1 = H$; $R^2 = H$ (**9**), Me (**10**), CF₃ (**11**), Ph (**12**);
 $R^1 = R^2 = Me$ (**13**).

The synthesis of PARV **9–13** was performed in DMF with the Pd(OAc)₂–P(Tol-*o*)₃–NEt₃ catalytic system at 100 °C for 20 h. In all cases two fractions, DMF-soluble and DMF-insoluble, were isolated from the reaction mixtures. High-temperature gel-permeation chromatography (GPC) of these fractions showed (Table 1) that the DMF-insoluble fractions (with the exception of non-substituted PARV **9**) have higher molecular weight. The fractions insoluble in DMF are soluble in *N*-methylcaprolactam at 140 °C, the molecular weight of the polymer being related to its solubility. Among the polymers synthesised, all substituted PARV **10–13** are more soluble than non-substituted **9**, the phenyl-substituted polymer **12** being the most soluble one. It is well soluble in chloroform and styrene.

Synthesis of PARV according to Scheme 1 was also performed with the reaction time extended to 48 h and chloroform used as a solvent.^{58–60} The reaction employed the 1,4-dibromides **8** with the following substituents $R^1 = H$, $R^2 = H$, Me, Ph, CF₃, F, NO₂; $R^1 = F$, $R^2 = CF_3$. In all cases, the PARV obtained comprised two fractions, a chloroform-soluble one and an insoluble one; the yield of the former was 0%–55%.

Additionally to the synthesis according to Scheme 1, two other approaches were used in order to obtain PARV with improved solubility.^{58–60} The first approach was to use substituted and non-substituted 4,4'-dibromobiphenyls; in the second, at least two haloarenes of different structures were used in the reaction with ethylene.

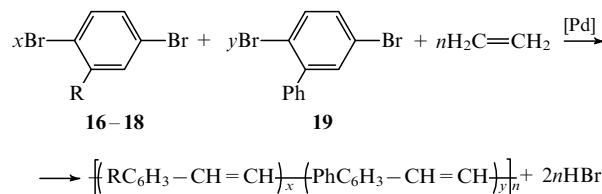
The former approach is based on the fact that aromatic rings in biphenyl fragments are not coplanar and can rotate with respect to one another.



$R = H$ (**14**), Me (**15**).

The introduction of substituents in dibromobiphenyl monomer results in enhanced non-coplanarity of these rings and, hence, lower length of conjugated segments in PARV chain. This change is reflected in the physical properties of the polymer. Thus the PARV **14** based on 4,4'-dibromobiphenyl does not melt and is insoluble in organic solvents; its colour is light-yellow. At the same time, PARV **15** based on 2,2'-dimethyl-4,4'-dibromobiphenyl is colourless, it is low-melting and dissolves well in chloroform and *N*-MP; its molecular weight measured using GPC is 10 700.

Reduced regularity of PARV structure, which is achieved when ethylene reacts with different substituted dibromobenzenes constitutes the basis of the second approach.



$R = H$ (**16**), Me (**17**), NO₂ (**18**).

Some properties of random copolymers prepared according to the second method⁵⁹ are presented in Table 2. Expectedly, the

Table 2. Some properties of random copolymers based on substituted *p*-dibromobenzenes **16–18** and 2,5-dibromobiphenyl **19**.⁵⁹

R	x	y	Yield, ^a (%)	T_g /°C	Fraction A ^b (%)	M_w^c	Solubil- ity ^d in <i>N</i> -MP at 150 °C
H	0.50	0.50	78	133	33	2030	<i>ps</i>
Me	0.50	0.50	93	154	67	4100	<i>s</i>
NO ₂	0.02	0.98	96	180	70	7490	<i>is</i>
	0.05	0.95	92	175	62	15 000	<i>ps</i>
	0.10	0.90	100	162	91	7800	<i>ps</i>
	0.20	0.80	95	152	78	8600	<i>ps</i>
	0.25	0.75	88	156	62	4800	<i>s</i>
	0.35	0.65	94	—	78	5400	<i>s</i>
	0.40	0.60	97	173	51	6750	<i>ps</i>
	0.50	0.50	96	—	48	3120	<i>ps</i>

^a Calculated without account of bromine content. ^b Fraction A is soluble in chloroform; percentage of the total yield of the polymer. ^c M_w for fraction A determined by GPC with polystyrene standard. ^d Hereinafter *s* denotes soluble; *is*, insoluble, and *ps*, partially soluble polymer.

Table 3. Some properties of the random copolymers **20** based on binuclear and condensed dibromoarenes prepared according to Scheme 2.⁵⁹

—Ar—	—Ar'—	x	y	Yield ^a (%)	Fraction A ^b (%)	M _w ^c	T _g /°C	Solubility in N-MP at 150 °C
		0.50	0.50	92	12	500	—	is
		0.50	0.50	87	68	1830	132	ps
		0.25	0.75	83	77	1070	135	ps
		0.50	0.50	50	92	9200	134	s
		0.25	0.75	71	88	6600	145	s
		0.50	0.50	75	88	5330	174	is

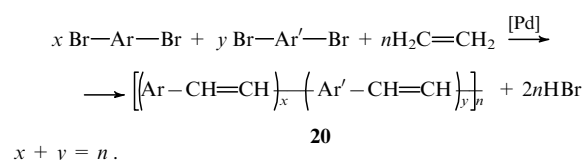
^a Calculated without account of bromine content. ^b Fraction A is soluble in chloroform; percentage of total yield of the polymer. ^c M_w for fraction A determined by GPC with polystyrene standard.

copolymers with different substituents in phenylene fragments often have a similar or improved solubility compared to corresponding homopolymers.

Analysis of the properties of copolymers based on dibromide **18** (homopolymer is insoluble) and 2,5-dibromobiphenyl **19** (soluble homopolymer) showed that they all are soluble, the solubility being nonlinearly dependent on the content of nitro-substituted phenylene groups (most soluble is the copolymer containing ~25% of such groups).

Copolycondensation of ethylene with binuclear and condensed dibromoarenes yields PARV **20**, which also have lower structural regularity (Scheme 2).

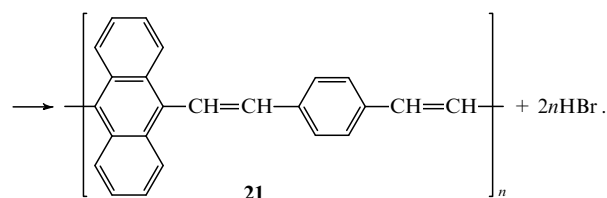
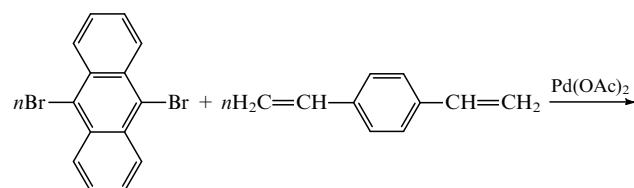
Scheme 2



The properties of copolymers **20** presented in Table 3 show that irregularity of the distances between vinylene groups does not noticeably affect solubility of copolymers, whereas introduction of alkyl substituents in initial aromatic compounds enhances solubility.

The synthesis of PARV by reaction of haloarenes with divinylaromatic compounds was considered in Refs 61–67.

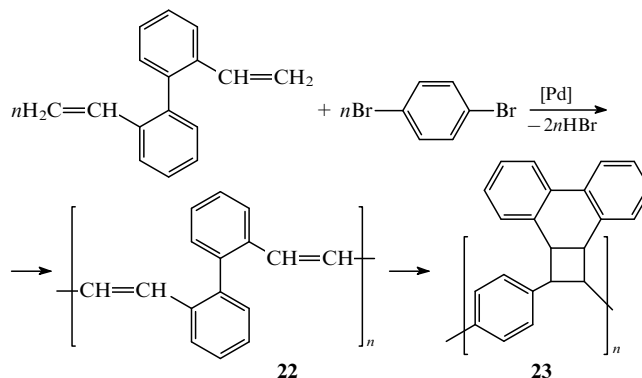
An attempt was made^{61,67} to obtain anthracene-containing PARV by the Heck's reaction in DMF at 90 °C with a palladium acetate–tris(*o*-tolyl)phosphine–triethylamine catalytic system; the reaction time was 24 h. The reactions of 9,10-divinylanthracene with various dihaloarenes did not produce the desired product, whereas reaction of 9,10-dibromoanthracene with *p*-divinylbenzene gave PARV **21** in nearly quantitative yield.



The solubility of PARV **21** in organic solvents is very low; therefore it precipitates from the reaction mixture in the course of polycondensation. This results in termination of the chain growth and formation of a low-molecular-weight product. This is confirmed by the data on the molecular weight of the polymer **21** (M_w = 1000) and bromine content (15.4%). In order to enhance solubility of PARV, 2-*tert*-butyl-9,10-dibromoanthracene was used as the initial dibromoanthracene. The oligomer based on it had higher molecular weight; the DMF-soluble fraction had M_w = 1300 and insoluble one, M_w = 1500.

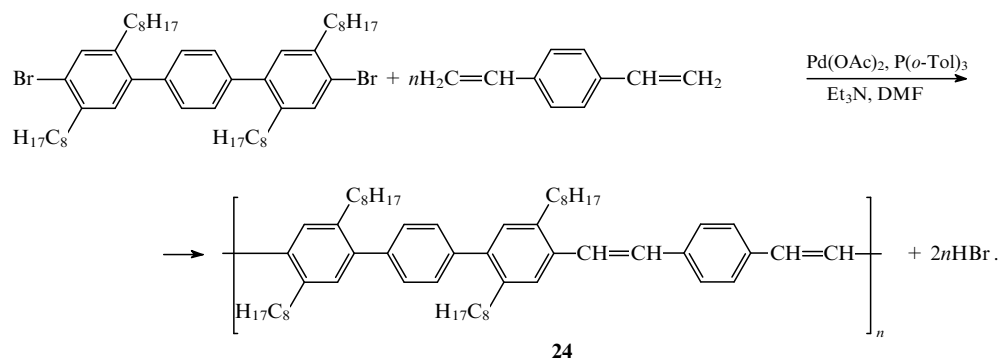
Photosetting PARV **22** were obtained by Müllen *et al.*⁶³ by the reaction of 2,2'-divinylbiphenyl with *p*-dibromobenzene (Scheme 3). Upon UV-irradiation of the polymer **22** in solution or in solid it is transformed into polymer **23** that incorporates dihydrophenanthrene and cyclobutane fragments.

Scheme 3



The PARV **24** that incorporates alternating phenylenebisvinylene and alkyl-substituted terphenylene units was prepared by the reaction of 4,4'-dibromo-2,2'',5,5''-tetraoctyl-*p*-terphenyl with *p*-divinylbenzene (Scheme 4).⁶⁴

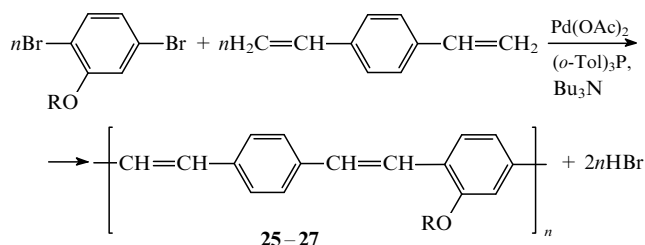
Scheme 4



According to DSC data, the glass transition temperature of the polymer **24** is -20°C . The polymer is very soluble in THF, chloroform and toluene; this is due to the presence of long aliphatic substituents, which loosen the polymer structure and reduce intermolecular interactions. Previously long alkyl substituents were introduced in initial monomers in order to produce soluble rigid-chain polymers^{68–70} (*viz.* poly-*p*-phenylenes). The GPC measurements of molecular-weight distribution showed that M_w of the polymer **24** is 4500 and polydispersity $M_w/M_n = 1.7$. These data further confirm that the molecular weights depend on their solubility in the reaction mixture; the molecular weight is always higher for the polymers having in their aromatic fragments substituents (*e.g.* aliphatic groups), which enhance their solubility.

Thermogravimetric analysis (TGA) of PARV **24** showed that decomposition of the polymer in N_2 starts at 420°C . The PARV **24** constituted a basic material for efficient light-emitting diodes (blue light).⁵⁹

Polyarylenes **25–27** incorporating side alkoxy groups were obtained in 70%–94% yield by reaction of *p*-divinylbenzene with 2,5-dibromo-1-alkoxybenzenes.⁶⁵



$\text{R} = \text{n-C}_6\text{H}_{13}$ (**25**), $\text{n-C}_{12}\text{H}_{25}$ (**26**), $\text{CH}(\text{C}_5\text{H}_{11})_2$ (**27**).

It has been shown previously that introduction of alkoxy substituents into initial monomers is an efficient means for reduction of glass transition and melting temperatures and enhancement of solubility of rigid-chain polymers.^{71,72} The solubility of alkoxy-substituted PARV depends on the size and

structure of a substituent. Thus PARV **25** is insoluble in organic solvents, the polymer **26** has a limited solubility in tetrachloroethane (TCE), and only PARV **27** ($M_n = 5400$) incorporating 1-pentylhexyl group is well soluble in TCE and chloroform; this is due to reduced (owing to steric hindrance) intermolecular interaction of the polymer chains.⁶⁵

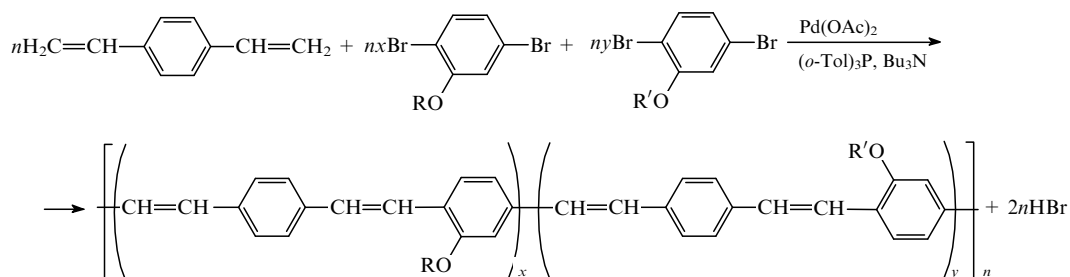
The synthesis of PARV **28**, which incorporate a stilbene chromophore with non-linear optical activity as a substituent (Scheme 5), is also described in Ref. 65. Some properties of the PARV synthesised are presented in Table 4. The polymers containing non-linear optical chromophore and unbranched alkoxy groups are insoluble in organic solvents. Possibly, this is related to the strong intermolecular interaction associated with the presence of large number of polar chromophore groups. Only copolymers containing 50%–70% of $\text{OCH}(\text{C}_5\text{H}_{11})_2$ -groups were soluble in TCE or mixtures of TCE with DMF. Similar to the majority of

Table 4. Some properties of PARV **28**.

R	x	y	Solubility	M_n	Yield (%)	T_g / $^{\circ}\text{C}$	T_d^a / $^{\circ}\text{C}$
without OR-groups	0	1	is	—	81	110	399
n-C ₆ H ₁₃	0.5	0.5	is	—	88	113	410
	0.1	0.9	is	—	68	112	399
n-C ₁₂ H ₂₅	0.5	0.5	is	—	81	98	396
	0.1	0.9	is	—	71	125	360
CH(C ₅ H ₁₁) ₂	0.7	0.3	s(TCE)	5000	82	90	370
	0.5	0.5	s(TCE, DMF)	5000	73	92	342
	0.1	0.9	is	—	89	105	387

^a According to DTGA data. Hereinafter T_d is measured in nitrogen atmosphere at the heating rate of $4^{\circ}\text{C min}^{-1}$.

Scheme 5



$\text{R} = \text{n-C}_6\text{H}_{13}$, $\text{n-C}_{12}\text{H}_{25}$, $\text{CH}(\text{C}_5\text{H}_{11})_2$;

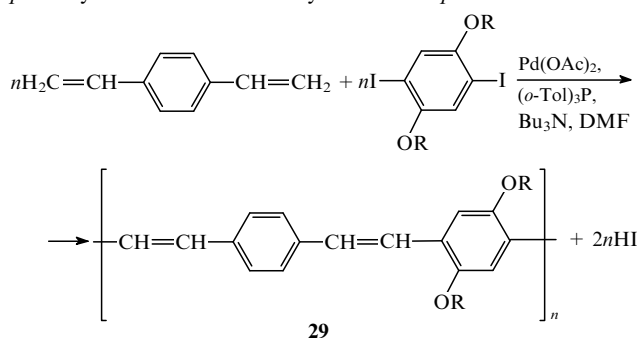
$\text{R}' = -(\text{CH}_2)_6-\text{N}(\text{CH}_3)-\text{C}_6\text{H}_4-\text{CH}=\text{CH}-\text{C}_6\text{H}_4-\text{S}-\text{C}(=\text{O})-\text{OMe}$.

PARV, these copolymers have moderate molecular weights ($M_n = 5000$).

Studies of the physical properties of these polymers showed that they possess photoinduced conduction and electrooptical activity but do not manifest photorefraction.

Some of the homo- and co-polymers synthesised have liquid-crystal properties and form nematic mesophases. This is related⁶⁵ to the rigidity of macromolecular backbones of PARV containing stilbene and distyrylbenzene fragments.^{73, 74}

Soluble and meltable PARV **29** with conjugated chains that have mesomorphic properties were obtained⁶⁶ by reaction of *p*-divinylbenzene with dialkoxy-substituted *p*-diiodobenzenes.



$\text{R} = \text{C}_n\text{H}_{2n+1}$ ($n = 4, 7, 8, 12, 16$).

All the polymers synthesised are well soluble in THF, chloroform, toluene and dichloroethane. This allowed determination of their molecular weight characteristics (Table 5) and some structural studies. The TGA data show that PARV **29** are stable in nitrogen atmosphere up to 430 °C and DSC shows that their glass transition temperatures (second-order transitions) are in the range of 33–46 °C and decrease with shorter side chains (Table 5). All DSC curves exhibit at least two transitions, which are related to melting of the side and backbone chains (Table 6), the distinct melting temperatures decreasing with longer side chains (nematic mesophases form at the temperatures above melting point).

Thermotropic liquid-crystalline PARV **30** incorporating mesogenic groups and spacers in their backbone chain were synthesised by reactions of *m*- and *p*-divinylbenzenes with diiodo-

Table 5. Some properties of PARV **29**.⁶⁶

R	M_n	M_w	Polydispersity	T_g /°C
C ₄ H ₉	8300	32 000	3.85	—
C ₇ H ₁₅	18 500	49 300	2.66	46
C ₉ H ₁₉	15 800	46 900	2.97	44
C ₁₂ H ₂₅	21 800	62 500	2.87	38
C ₁₆ H ₃₃	18 700	53 900	2.88	33

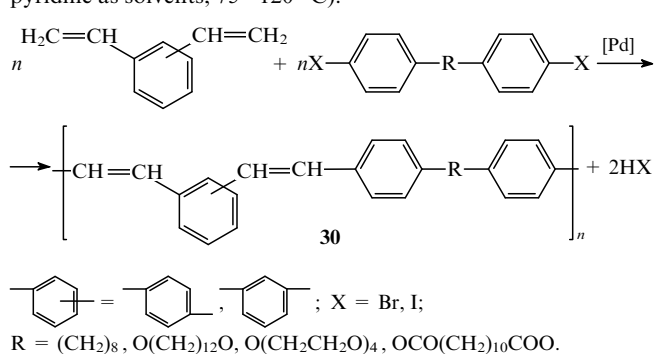
Table 6. DSC data for alkoxy-substituted PARV **29**.⁶⁶

R	T_1 /°C	ΔH_1 /J deg ⁻¹	T_2 /°C	ΔH_2 /J deg ⁻¹	T_3 /°C	ΔH_3 /J deg ⁻¹
C ₄ H ₉	see ^a	see ^a	239.0	106.0	325.0	see ^a
C ₇ H ₁₅	73.8	2.48	see ^b	see ^b	see ^a	see ^a
C ₉ H ₁₉	82.0	2.25	see ^b	see ^b	see ^a	see ^a
C ₁₂ H ₂₅	69.1	4.90	152.0	10.24	see ^a	see ^a
C ₁₆ H ₃₃	66.4	2.75	103	8.52	133.0	103

Note. The temperatures and enthalpies of phase transitions are given. Subscript 1 refers to melting of side chains; 2, to the melting of backbone chains, and 3, to nematic/isotropic transition.

^a Transition was not observed. ^b The temperature and enthalpy of the transition were not determined due to cross-linking of the macromolecules.

and dibromo-arylenes containing various bridge groups (DMF or pyridine as solvents, 75–120 °C).⁶⁷



Depending on the nature of the monomers used, the polycondensations were either homogeneous or heterogeneous. Iodoorganic compounds proved to be more reactive than bromoaromatics [the latter required higher concentrations of the catalysts and higher temperatures (to 120 °C)]. The properties of PARV obtained are presented in Table 7.

Table 7. Some properties of PARV **30**.⁶⁷

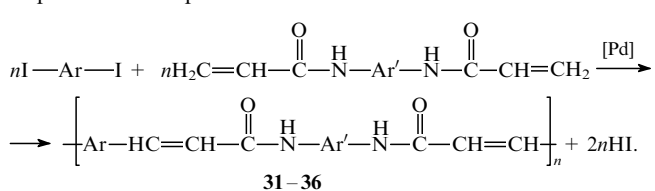
C_6H_4	$-\text{R}-$	Yield (%)	Content of halide (%)
I-C₆H₄-R-C₆H₄-I			
-(1,3-C ₆ H ₄)-	-O-(CH ₂ CH ₂ O) ₄ -	94 ^a	1.08
-(1,4-C ₆ H ₄)-	-O-(CH ₂ CH ₂ O) ₄ -	99	2.74
-(1,3-C ₆ H ₄)-	-O-(CH ₂) ₁₂ -O-	73	0
-(1,4-C ₆ H ₄)-	-O-(CH ₂) ₁₂ -O-	96	8.71
Br-C₆H₄-R-C₆H₄-Br			
-(1,3-C ₆ H ₄)-	-OCO-(CH ₂) ₁₀ -COO-	69 ^b	3.31
-(1,4-C ₆ H ₄)-	-OCO-(CH ₂) ₁₀ -COO-	81	6.72
-(1,3-C ₆ H ₄)-	-(CH ₂) ₈ -	69	3.43
-(1,4-C ₆ H ₄)-	-(CH ₂) ₈ -	96	2.56

^a $M_w = 14600$, $M_w/M_n = 1.48$. ^b Logarithmic viscosity in *p*-chlorophenol–chloroform solution is 0.51 dl g⁻¹.

The polymers based on *p*-divinylbenzene are insoluble in organic solvents, whereas PARV based on *m*-divinylbenzene and dihaloarenes incorporating ethylene oxide and ester groups are soluble in *p*-chlorophenol and in a mixture of CF₃COOH with CHCl₃; the molecular weights of soluble polymers were measured using GPC (they varied within 1400–14 600).

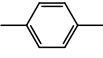
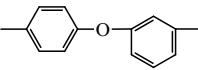
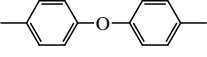
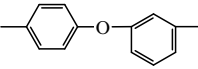
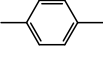
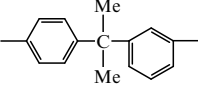
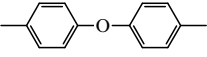
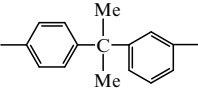
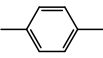
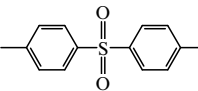
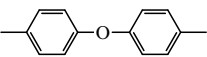
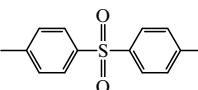
DSC and optical microscopy showed that PARV **30** manifest thermotropic liquid crystallinity. The mesophases of the polymers based on *m*-divinylbenzene and containing ether and ester groups have the smectic texture.

Reactions of unsaturated bisamides with dihaloarenes belong to the same type of processes.^{75–85} The synthesis of polycinnamamide **31** from bisacrylamide and aromatic diiodide in the presence of palladium complexes is studied in most detail.



The polycondensations were performed in various polar aprotic solvents [DMF, dimethylacetamide (DMAA), *N*-MP, DMSO, hexamethylphosphoramide, 1,3-dimethyl-2-imidazoli-

Table 8. Properties of polycinnamamides **31–36**.

Com- pound	–Ar–	–Ar'–	Yield (%)	$\eta_{\log}$ /dl g ⁻¹	T_g /°C	T_d (10%) /°C	
						N ₂	air
31			99	1.51	–	445	450
32			99	2.60	232	445	445
33			97	1.32	269	395	385
34			94	0.89	238	395	395
35			97	0.26	–	–	–
36			96	0.22	–	–	–

done]; the best results were obtained in DMF. Palladium acetate, palladium chloride and their combinations with triphenylphosphine, tris(*o*-tolyl)phosphine and 1,4-bis(diphenylphosphino)butane were tested as the catalysts. The polymers with highest viscosity were prepared with a Pd(OAc)₂–P(*o*-Tol)₃ (1 : 4) catalytic system in the presence of 1,8-bis(dimethylamino)naphthalene as a base. The reaction was performed at 100 °C for 4 h; when the synthesis temperature was increased to 110 °C, the reaction was accompanied by gelation. Polycinnamamides **31–34** were prepared in homogeneous conditions. High logarithmic viscosities $\eta_{\log}$ of the solutions indicate that the reaction products are high polymers (Table 8). Thus M_n and M_w of polycinnamamide **32** having viscosity of 2.60 dl g⁻¹ are 93 000 and 488 000, respectively. Polycinnamamides **35** and **36** were prepared in heterogeneous conditions and have low logarithmic viscosities.

Polycinnamamides **31–36**, with few exceptions, are soluble in pyridine, DMSO, DMAA, *N*-MP and DMF. Strong transparent films were casted from their solutions in DMF.

According to DTG data, the temperatures of decomposition (10% weight loss) for the polycinnamamides are in the range 380–450 °C, the polymers incorporating ether groups being more heat-resistant than those with isopropylidene groups.

The presence of double carbon–carbon bonds in the backbone chains of the polycinnamamides predetermines their capability of curing when heated (>250 °C) or subjected to UV irradiation.

An attempt was undertaken⁸² to obtain polycinnamamides under conditions of heterophase catalysis using a palladium–graphite catalyst (Pd–Gr). Such catalysts prepared by metal exchange in potassium-intercalated graphite⁸⁴ are known to possess high activity in hydrogenation of alkenes,⁸⁵ Heck's reaction⁸⁶ and nucleophilic substitution *via* π -allyl complexes.⁸⁷

The synthesis of polycinnamamide **32** was performed in the presence of a Pd–Gr–tributylamine catalytic system in DMF at 100 °C for 20–40 h. Under such conditions, even without a cocatalyst, polymers having logarithmic viscosity of 0.9 dl g⁻¹ (which corresponds to the molecular weight of 100 000) can be prepared. Comparison of the results of syntheses of the polycinnamamide on Pd–Gr catalysts and other Pd-containing catalysts is given in Table 9.

Table 9. Comparison of the results of syntheses of polycinnamamide **32** with various palladium catalysts.⁸²

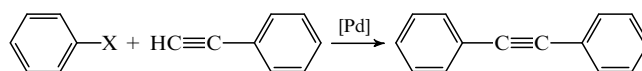
Catalyst	Reaction time /h	Yield (%)	$\eta_{\log}$ /dl g ⁻¹
Pd–Gr	4	90	0.25
	20	95	0.90
Pd–Gr–P(Tol- <i>o</i>) ₃	20	96	0.81
Pd–C	20	94	0.69
Pd(OAc) ₂ –P(Tol- <i>o</i>) ₃	4	95	1.11

According to the results obtained, the heterogeneous catalytic reaction proceeds slower than the homophase reaction in the presence of Pd(OAc)₂. The reaction on a Pd–Gr catalyst not only has the common advantage of heterophase catalysis (*i.e.*, ease of separation of the catalyst from the reaction products) but also yields polycinnamamides with lower polydispersity and lower palladium content, as compared to similar polymers prepared with Pd(OAc)₂.

Generally, the method developed for heterophase synthesis of polycinnamamides^{81,82} is simpler than the conventional procedure⁸⁸ based on the reaction of biscinnamic acids or their derivatives with diamines.

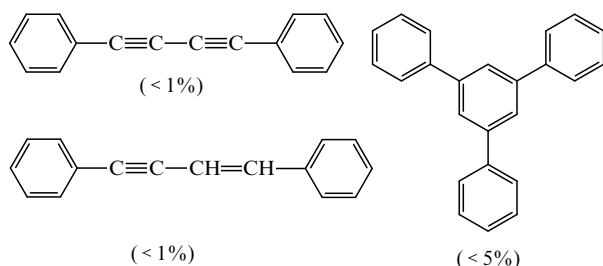
III. Synthesis of polyaryleneethynlenes

The synthesis of PARE is based on the reaction of terminal acetylene groups with a haloaromatic compound.



This reaction is performed in the presence of copper(I) iodide, a base and a palladium salt as a catalyst. Most often PdCl₂(PPh₃)₂ is used as catalyst and DMAA and DMF as solvents, although THF⁸⁹ and pyridine were also successfully used.

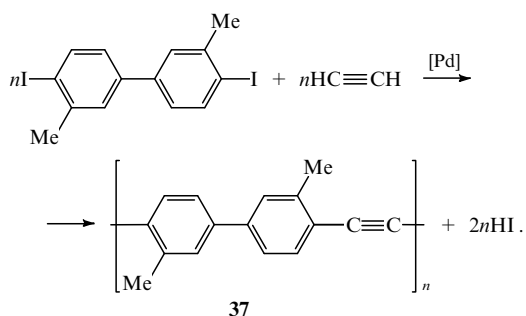
The reaction of iodo(or bromo)benzene with phenylacetylene³⁹ catalysed by PdCl₂(PPh₃)₂ complex also gives by-products,⁴² *viz.* diyne, enyne and 1,3,5-triphenylbenzene.



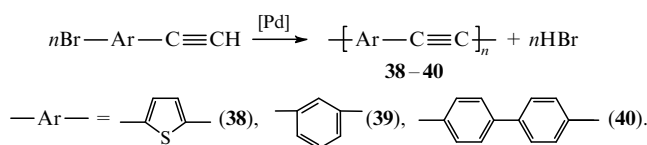
The yields of these compounds, which strongly affect the polycondensation processes, can vary, depending on the reaction conditions;⁴² this necessitates the search for the optimal conditions for each particular polycross-coupling.

Similar to PARV, polyaryleneethynylenes have been prepared *via* three different ways, namely, by reaction of acetylene with dihaloarenes, by homopolycondensation of haloarylacetylenes and by reaction of diethynylaromatic compounds with dihaloarenes.

The reactions of acetylene with dihaloarenes, unlike the corresponding reactions with ethylene, did not find wide application. Thus the reaction of 4,4'-diiodo-3,3'-dimethylbiphenyl with acetylene⁴² yields the product **37** with low molecular weight due to its insolubility in organic solvents. When heated, the oligomer **37** gives a red anisotropic melt.



Homopolycondensation reactions of haloarylacetylenes (AB-type monomers) were studied in detail by Marvel *et al.*^{90–92} Homopolycondensations of 2-ethynyl-5-bromothiophene,⁹⁰ 3-bromophenylacetylene⁹² and 4-bromobiphenylacetylene⁹¹ were performed with the use of a $(\text{Ph}_3\text{P})_2\text{PdCl}_2\text{--PPh}_3\text{--CuI}$ catalytic system; the solvent used was triethylamine–pyridine mixture.^{32, 36, 39, 93–95}



The choice of this catalytic system was based on the high yield of the products of cross-coupling.^{39, 95} Note, however, that this catalytic system increases contribution of a side reaction, because phenylacetylene polymerises efficiently on this catalyst.⁹⁶

Homopolycondensations were carried out at 90 °C for 2.5–46 h and yielded low-molecular-weight PARE **38–40** (Table 10). The IR spectra of PARE **38–40** did not show the absorption maxima corresponding to terminal ethynyl groups. This is believed⁹¹ to result from oxidative coupling of acetylene groups, occurring in parallel with the major reaction. This side reaction has been described previously.^{97, 98}

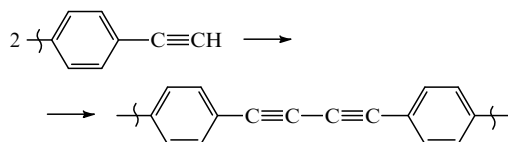


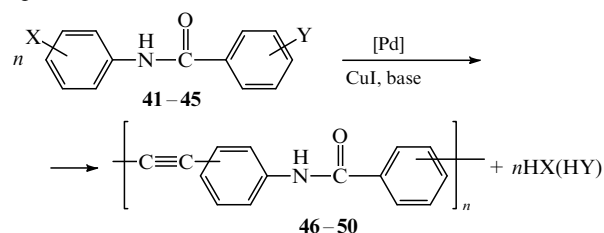
Table 10. Conditions of synthesis and properties of PARE **38–40**.^{90–92}

Compound	Composition of solvent (NEt ₃ :Py)	Reaction time /h	Conversion (%)	Fraction A ^a (%)	M _w	M _n	Content of Br (%)
38	6:4	4.5	23.1	–	2170	1140	13.25
	6:4	10	28.6	–	1470	1030	12.12
	6:4	15	27.4	–	1440	1020	14.46
39	25:17	15	51.2	–	1800	1450	8.86
	17:25	15	37.2	–	1650	1270	9.11
	26:17	46	40.0	–	2000	1500	8.91
40	15:10	2.5	82.6	5.6	2560 ^b	1700 ^b	6.86
	15:10	5	89.9	3.1	2480 ^b	1750 ^b	6.18
	15:10	10	91.7	3.3	2260 ^b	1630 ^b	7.84
	15:10	15	94.2	4.6	2230 ^b	1580 ^b	7.22
	15:10	30	95.6	2.8	2780 ^b	2050 ^b	7.11
	12.5:12.5	15	92.8	2.9	2440 ^b	1800 ^b	6.79
	3:22	15	90.6	6.5	3160 ^b	1940 ^b	6.81

^a Fraction A is soluble in chloroform. ^b Determined for soluble fractions.

Thermogravimetric studies of PARE **38–40** showed that they are quite stable up to 300 °C, the weight loss in 20 h was less than 10%. The polymers did not melt at 300–400 °C but they gradually darkened and after 20 h of high-temperature ageing turned into black powders.

Synthesis of PARE **46–50** was also based on homopolycondensation of the AB-type monomers **41–45** incorporating amide groups.⁹⁹



41, 46: X = *p*-Br, Y = *p*-C≡CH; **42, 47:** X = *m*-Br, Y = *p*-C≡CH; **43, 48:** X = *m*-C≡CH, Y = *p*-Br; **44, 49:** X = *m*-C≡CH, Y = *p*-I; **45, 50:** X = *m*-C≡CH, Y = *m*-I.

Depending on the nature of the monomers, the reactions proceeded either heterogeneously or homogeneously and the yield of polyaryleneethynyleneamides was 96%–100% (Table 11). When bromine-containing monomers were used, low-molecular-weight products were obtained ($\eta_{\log}$ = 0.12–0.18 dl g^{–1}), whereas polycondensation of the iodine-containing monomer **45** yielded polymer **50** with logarithmic viscosity of

Table 11. Conditions of synthesis and some properties of polyethynyleneamides **46–50**.⁹⁹

Initial monomer	Reaction temperature /°C	Reaction time /h	Yield (%)	$\eta_{\log}$ /dl g ^{–1}
41	100	4	100	–
42	100	4	99	0.12
43	100	4	100	0.18
44	100	4	100	–
45	100	4	96	0.43
	80	4	95	0.18
	120	4	100	–
	100	1	96	0.16

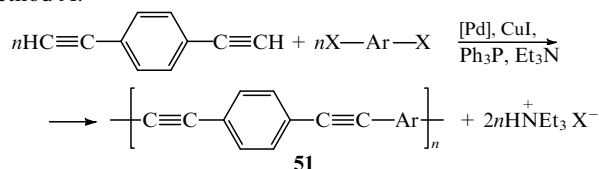
0.43 dl g⁻¹. This result agrees well with the data of Refs 43, 100, which reported higher activity of aryl iodides compared to aryl bromides in palladium-catalysed reactions of oxidative addition.

Studies of solubility of the polymers synthesised showed that simultaneous introduction of amide and *m*-phenylene groups in PARE results in substantially improved solubility of these polymers. Thus high-molecular-weight polymer **50** dissolves in DMF, DMAA, *N*-MP, DMSO, *m*-cresol and pyridine.

GPC studies of this polymer showed that its M_w is 108 000 and polydispersity $M_w/M_n = 16.4$, in other words, the polymer has broad molecular-weight distribution. According to TGA data, the temperature of beginning of the decomposition and that of 10% weight loss of PARE **50** are 315 and 350 °C, respectively. DSC showed that an exothermic peak is observed near 270 °C; it is related to the polymer curing *via* the ethynyl groups incorporated in the backbone chains of the macromolecules.

The majority of studies considered synthesis of PARE by reactions of dihaloarenes with diethynylarenes. First works in the field were published in the early 90s.^{101, 102} The polyaryleneethynylenes **51** were prepared using two methods.

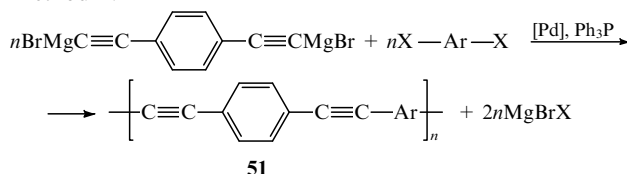
Method A.



–Ar–	X	Yield of 51 (%)
	Br	79
	I	97
	Br	84
	Br	93
	Br	95

The reactions were carried out for 1–3 h at 80–90 °C in an organic solvent (*e.g.*, toluene)¹⁰² in the presence of CuI and PPh₃. Pd(PPh₃)₄ or PdCl₂(PPh₃)₂ (up to 10 mol.%) were used as catalysts.

Method B.

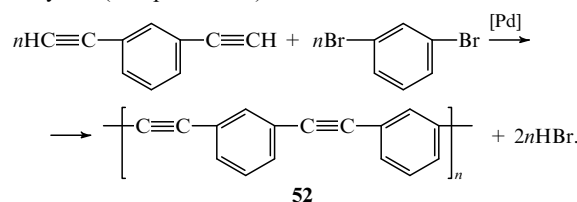


–Ar–	X	Yield of 51 (%)
	I	97
	Br	82

The reactions were carried out in THF for 2–3 h at 60–70 °C in the presence of Pd(OAc)₂ and PPh₃ or Pd(PPh₃)₃.

All the polymers **51** had high crystallinity but were poorly soluble. Therefore their molecular weights could be estimated only on the basis of halide content, which was substantial; most probably the molecular weights were in the range of 1400–4000.

PARE **52** was prepared by the reaction of *m*-dibromobenzene and *m*-diethynylbenzene;⁹¹ this polymer has the structure close to that of the products of homopolycondensation of *m*-bromophenylacetylene (compounds **39**).⁹⁴



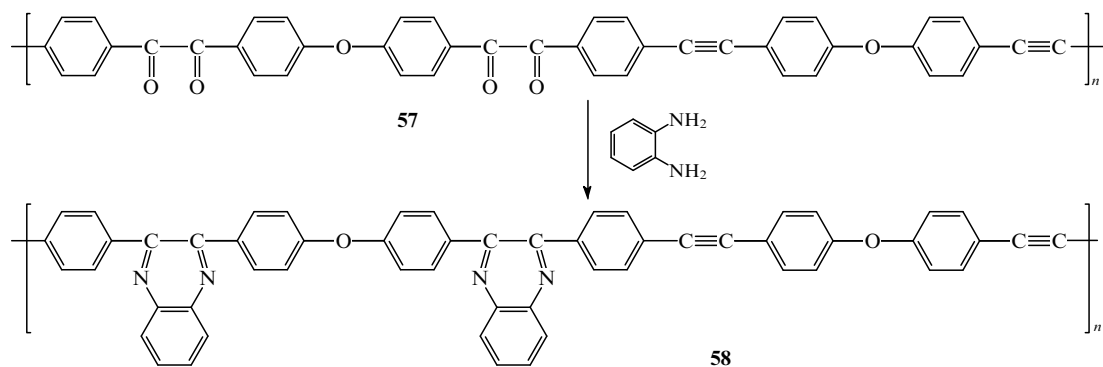
The synthesis of polymer **52** was carried out under the same conditions as those for the homopolycondensation of *m*-bromophenylacetylene. The polymer obtained had somewhat higher molecular weight ($M_w = 3000$). Note that the molecular weight of the polymer determined by means of GPC refers to its soluble fraction (~6%). Generally, this PARE has a very limited solubility. When *p*-dibromobenzene is used as the haloarene, the PARE formed is completely insoluble in organic solvents.

In order to prepare PARE having higher molecular weight and improved solubility, Hergenrother *et al.*¹⁰³ used monomers with bridge groups, the ‘activated’ dibromoaromatic compounds. The solvent used was DMAA. However, virtually all PARE **53–57** (Table 12) precipitated from the reaction solutions after

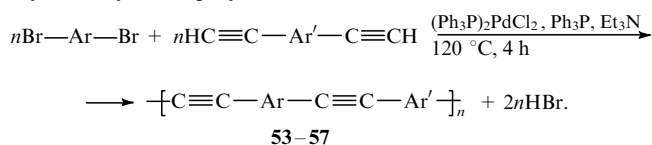
Table 12. Structure and some properties of PARE **53–57**.

PARE	–Ar–	–Ar'–	η_{log}	T_g^a / °C	T_{endo}^b / °C	T_{exo}^c / °C
53			see ^d	173	–	355
54			see ^d	–	–	343
55			see ^d	–	–	> 350
56			0.28	143	247	320
57			0.27	–	267	333/375

^a Glass transition temperature determined by DSC at the heating rate of 20 deg min⁻¹; ^b T_{endo} is the melting temperature of crystallites (according to DSC data); ^c T_{exo} is the temperature at which reaction of acetylenic groups starts; ^d PARE are insoluble in TCE, DMAA and *m*-cresol.



several minutes of stirring at 100–120 °C; this is related to the crystallinity of the polymers.

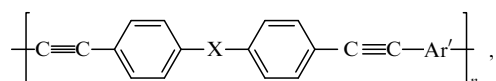


The investigation of PARE **53–57** by means of DSC revealed that they manifest endothermic peaks associated with the melting of crystallites and when the polymers are heated they show exothermic effects related to cross-linking *via* the disubstituted acetylenic groups (Table 12).

The polymers based on 4,4'-diethynyldiphenyl ether and dibromides such as 4,4'-bis(4-bromobenzyl)- and 4,4'-bis(3-bromobenzyl)diphenyl ether have limited solubility in TCE in which their viscosity was examined.

The polyaryleneethynylene **57** yields compound **58**, which contains quinoxal-2,3-diyl fragments, upon treatment with *o*-phenylenediamine in TCE (Scheme 6). According to the data of X-ray diffraction,¹⁰³ the polymer **58** having $T_g = 190\text{ }^{\circ}\text{C}$, had lower crystallinity than the initial PARE and correspondingly was better soluble in DMAA.

PARE of the type,



which have the structure and properties close to those of the compounds described in Ref. 103, have been prepared analogously.¹⁰⁴ The polycondensation was carried out in DMAA at 90 °C (in the presence of triethylamine) or at 120 °C (in the presence of tri-*n*-butylamine) for 4 h with a $\text{PdCl}_2(\text{PPh}_3)_2\text{--PPh}_3$ catalytic system (Table 13).

The PARE obtained are insoluble in organic solvents and decompose in H_2SO_4 ; therefore, their molecular weights were determined from elemental analysis under the assumption that each macromolecule has one terminal bromine atom. The differential thermogravimetry in N_2 shows a small weight loss near 280 °C and less than 5% at 400 °C. The data of DSC indicate that there is a substantial exothermic effect at 250–280 °C; it can be related to thermal cross-linking of the polymer *via* the acetylenic groups.

Similar approach to the preparation of PARE was employed by Rusanov *et al.*^{105–107} In order to enhance solubility and to increase molecular weights of the polymers, the monomers containing various bridge groups or aromatic substituents were employed. Thus reaction of 4,4'-diiododiphenyl ether with *p*-diethynylbenzene, 4,4'-diethynyldiphenyl ether and 1,2-bis[4-(4'-ethynylphenoxy)phenyl]-*o*-carborane in DMF at 100 °C during 4 h yielded predominantly products of cross-coupling.¹⁰⁵

Some properties of the PARE obtained are presented in Table 14. Among the polymers **59–61**, the carborane-containing

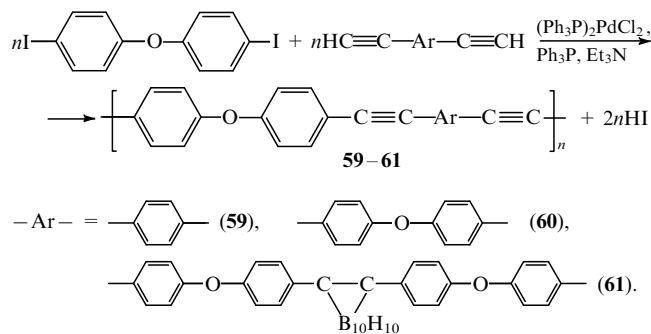
Table 13. Conditions of synthesis¹⁰⁴ and some properties of PARE of type

$$\left[\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{X}-\text{C}_6\text{H}_4-\text{C}\equiv\text{C}-\text{Ar}' \right]_n.$$

–X–	–Ar'–	Molecular weight ^a	T_{exo} , /°C	Content of Br (%)
None		500 ^b	–	15.30
–O–		600 ^c	–	13.36
–C(O)–		1000	–	7.83
–O–		550	–	13.83
–C(O)–		1000	260	7.66
None		500	–	15.71
–O–		700	260	11.25
–C(O)–		1100	280	7.00

Note. Solvent is DMAA, temperature is 120 °C.

^a Calculated on the basis of elemental analysis. ^b Solvent is DMAA, temperature is 90 °C. ^c Solvent is *N*-MP, temperature is 120 °C.



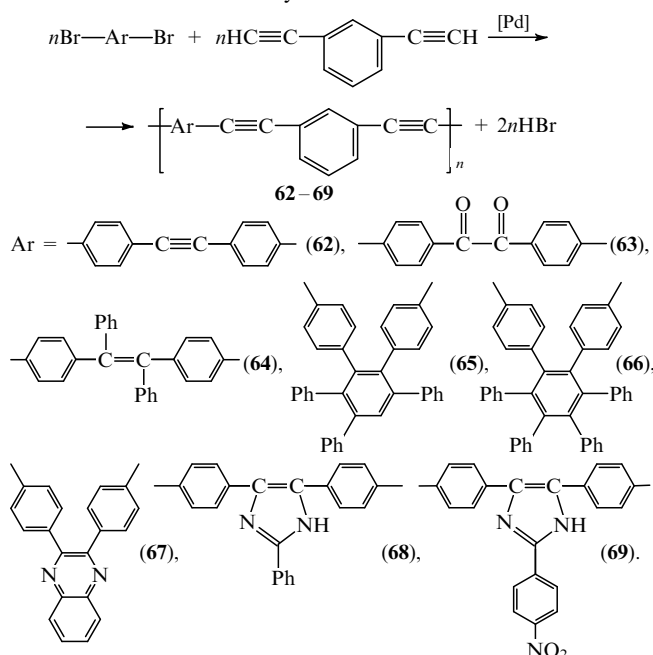
compound **61** is the best soluble one; it is soluble in chloroform and amide solvents. This agrees well with the existing notion^{108–110} that carborane groups positively affect solubility of condensation polymers.

Table 14. Some properties of PARE **59–61**.¹⁰⁹

PARE	Yield (%)	Molecular weight ^a	T_g /°C	T_d^b /°C	Content of I (%)
59	98	820	250	390	15.68
60	82	2400	245	450	5.36
61	80	5500	200	480	0.50

^a According to the data of ebullioscopy in chloroform or sedimentation in *N*-MP. ^b The temperature of 10% weight loss, DTGA.

A much wider variety of dihaloarenes was used^{106, 107} for the synthesis of PARE by reaction of 1,3-diethynylbenzene with various carbo- and hetero-cyclic dibromides.



The reactions were carried out in DMAA at 90 °C for 10 h with the $\text{PdCl}_2(\text{PPh}_3)_2$ – PPh_3 – CuI – Et_3N catalytic system. The data presented in Table 15 show that certain phenyl-substituted PARE are soluble in amide solvents (DMF, DMAA, *N*-MP); this agrees well with the inference¹¹¹ that phenyl substituents have a positive effect on the solubility of polyheteroarylenes. Nevertheless, the degree of polymerisation of these PARE calculated on the basis of Br content did not exceed 2–3. It should be noted that the degree of polymerisation of insoluble PARE obtained from dibromides activated by α -diketone, acetylene, ethylene groups and quinoxal-2,3-diyl fragments is also small (3–5). Apparently, solubility of the target compounds in the reaction mixture is a necessary but

Table 15. Properties of PARE **62–69**.¹⁰⁹

PARE	Yield (%)	η_{lim} /dl g ^{−1} (DMF)	Content of I (%)	n^a	Solubility
62	72	–	10.65	4	–
63	70	–	12.67	5	–
64	74	–	8.35	4	–
65	72	0.06	16.09	2	DMF, DMAA, <i>N</i> -MP
66	74	0.08	11.21	2	–
67	61	–	12.01	3	DMF, DMAA, <i>N</i> -MP
68	76	0.09	16.99	3	DMF, DMAA, <i>N</i> -MP
69	74	0.07	13.21	3	DMF, DMAA, <i>N</i> -MP

^a Calculated on the basis of elemental analysis.

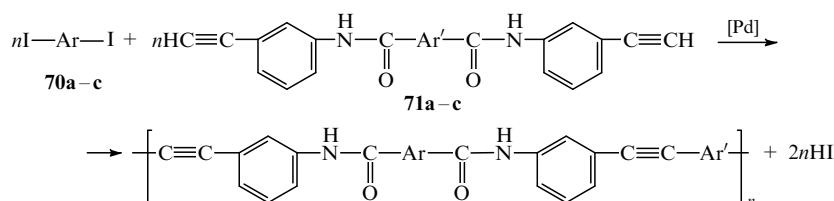
not sufficient condition for synthesis of high-molecular-weight products.

Amide groups were introduced into PARE macromolecules¹¹² in order to make them soluble in organic solvents; it has been shown previously⁹⁹ that in a number of cases this approach gives the desired result. Synthesis of such PARE was performed under usual conditions. In all cases, a small excess of bisethynylarenes was used; this resulted in formation of polymers with improved viscous properties (Scheme 7).

The course of polycondensation depends on the structure of diiodide **70** used. At 1×10^{-3} mol litre^{−1} concentration, polycondensation of *p*-diiodobenzene (**70a**) and 4,4'-diiododiphenyl ether (**70b**) with bisethynylarenes in DMAA proceeded heterogeneously and at half that concentration, homogeneously. Following isolation, majority of the polymers lost their solubility. The polycondensation of 4,4'-diiododiphenyl sulfone (**70c**) always proceeded homogeneously and the polymers obtained were well soluble in DMAA, DMF, *N*-MP, DMSO, *m*-cresol and *o*-chlorophenol.¹¹² Note that enhanced solubility of diphenyl sulfone-containing polymers, as compared to diphenyl ether-containing, and virtual no effect of diphenylhexafluoroisopropylidene groups on their solubility is quite unusual and falls outside the general structure–solubility dependence in the series of condensation polymers.¹¹³ The properties of the polymers obtained are presented in Table 16. Thus prepared polymers do not show any pronounced glass transition and in TGA experiments in nitrogen atmosphere do not lose weight until 300 °C. At 280 °C, the polymers cross-link *via* acetylenic groups yielding insoluble systems.

The most versatile and reliable method for enhancing solubility of PARE (similar to PARV) is the introduction of long-chain aliphatic substituents into their macromolecules.^{114–122} Schulz *et*

Scheme 7



(a): Ar = 1,4- C_6H_4 , Ar' = 1,3- C_6H_4 ;

(b): Ar = 4,4'-(C_6H_4 –O– C_6H_4), Ar' = 5-Bu¹-1,3- C_6H_3 ;

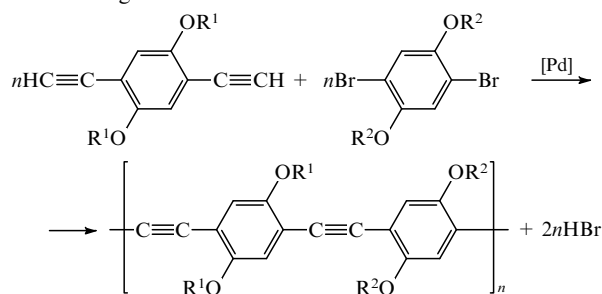
(c): Ar = 4,4'-(C_6H_4 – SO_2 – C_6H_4), Ar' = 4,4'-(C_6H_4 –C(CF_3)₂– C_6H_4).

Table 16. Some properties of PARE based on diiodides **70a–c** and bisethynylarenes **71a–c**.¹¹²

Bis-ethynyl-arene	Diiodide	Properties of the polymer			
		η_{log} /dl g ⁻¹ (DMAA, 30 °C)	M_w	M_w/M_n^a	T_d (10%) ^b /°C
71a	70a	—	—	—	365 (450)
	70b	—	—	—	370 (450)
	70c	—	—	—	350 (455)
71b	70a	0.72	—	—	355 (465)
	70b	0.43	—	—	—
	70c	—	—	—	—
71c	70a	0.33	17000	1.6	370 (435)
	70b	0.41	26500	1.6	370 (435)
	70c	0.29	12500	1.6	325 (460)

^a Determined by GPC. ^b The temperatures of the start of decomposition and 10% weight loss as determined by DTGA in air at the heating rate of 10 deg min⁻¹.

*al.*¹¹⁴ carried out synthesis of alkoxy-substituted PARE according to the following scheme



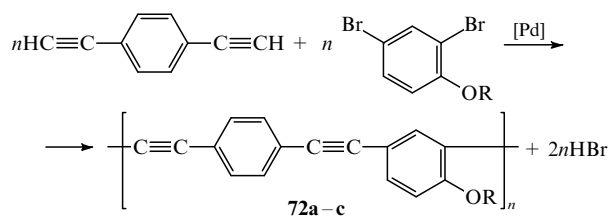
$R^1, R^2 = C_4H_9, C_6H_{13}, C_{11}H_{23}, C_{14}H_{29}, C_{18}H_{37}$.

1,4-Diethynylbenzene, 9,10-dibromoanthracene and *n*-alkyl-3,6-dibromocarbazoles were also used for the synthesis of PARE. All the polymers obtained were coloured from yellowish-orange to brown-red and manifested intense fluorescence in aromatic solvents.

The freshly prepared alkoxy-substituted PARE are soluble in boiling toluene, xylene or carbon disulfide. However, after drying *in vacuo* at 30–40 °C only polymers with long side chains ($R^1, R^2 = C_{14}H_{29}$ or $C_{18}H_{37}$) retain solubility. The polymer with $R^1 = R^2 = C_{18}H_{37}$ has the highest solubility (up to 3 g litre⁻¹ in hot toluene). The molecular weight of this polymer determined using GPC and osmometry is 8500–10 000; this corresponds to a degree of polymerisation within the range 9–15. This polymer is a meltable product that forms a transparent viscous melt at ~100 °C. At temperatures ≥170 °C, the polymer cross-links. Films with moderate mechanical properties were prepared from its solution.

DTGA of alkoxy-substituted PARE showed that their decomposition in nitrogen starts at 420 °C. In air decomposition proceeds in two stages, the first stage (70% weight loss) being associated with the cleavage of the side chains and the second, with oxidation of the backbone chains of the polymer.

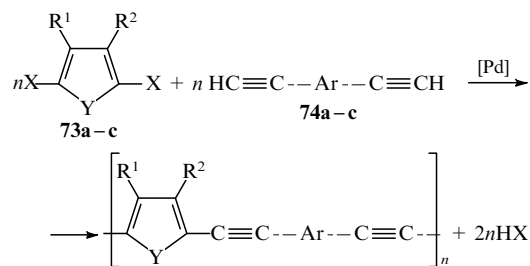
The alkoxy-substituted PARE **72a–c** with *m*-phenylene groups were obtained by reaction of 1,4-diethynylbenzene with 1-alkoxy-2,4-dibromobenzenes.¹¹⁵



$R = C_{16}H_{33}$ (**a**), $C_{18}H_{37}$ (**b**), $C_{22}H_{45}$ (**c**).

The yields and processibility of the products can be improved through an increase in the length of the substituents. Thus polymer **72c** is soluble in chloroform, benzene, THF, DMF and CS₂; its molecular weight (GPC in DMF) is 40 000; this provides a possibility of casting a good quality film from its chloroform solution.

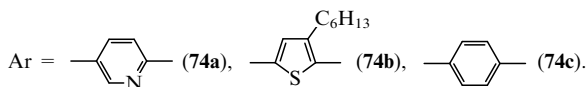
Synthesis of PARE incorporating heterocycles in their backbone chains was investigated in a number of studies.^{116–119}



73a: X = I, Y = S, $R^1 = H, R^2 = n-C_6H_{13}$;

73b: X = Br, Y = Se, $R^1 = R^2 = H$;

73c: X = Br, Y = S, $R^1 = R^2 = NO_2$;



The syntheses were carried out in anhydrous toluene according to the method described in Ref. 102 (Table 17). The polyaryleneethynyls based on diethynylpyridine **74a** and dihalides **73b** and **73c** are soluble only in HCOOH, whereas based on **73a** polymer incorporating hexylthiophene fragments is soluble in CHCl₃, CH₂Cl₂, THF, DMF and toluene. This indicates that alkyl substituents positively influence the solubility of PARV and PARE. The choice of 2,5-diethynylpyridine was based on the solubilising effect of pyridine-2,5-diyl groups on rigid-chain polymers.^{123, 124}

Table 17. Conditions of synthesis and molecular weights of PARE based on compounds **73** and **74**.

Initial compounds		Conditions of synthesis				Yield (%)	M_w^a
		Pd(PPh ₃) ₄ (mol. %)	CuI (mol. %)	T /°C	t /h		
73a	74a	1	2	110	2.5	100	4.8
	74a	1	2	50	1.5	100	4.3
	74b	5	4	60	5	88	1.9
	74c	1	2	110	2	93	0.96
73b	74a	2	5	60	2	100	—
73c	74a	2	2	60	19	86	9.6 ^b

^a Determined using light scattering in chloroform. ^b Light scattering in HCOOH.

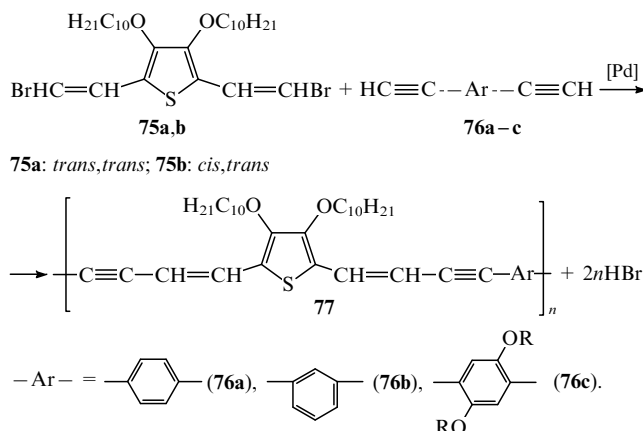
Virtually all the PARE obtained had high molecular weights. Strong films with non-linear third-order optical sensitivity $\chi^{(3)} = 5 \times 10^{-11}$ (cgs) were prepared from their solutions. All the compounds have high degrees of depolarisation ($\rho_v = 0.005-0.034$), which, nevertheless, are much lower than $\rho_v = 0.33$ observed for rigid-chain poly(pyridine-2,5-diyl) with the polymerisation degree of 50.^{122, 123} The polymers manifest fluorescence in solutions; $\lambda_{\max}$ in their spectra are shifted to the long-wave region.

Polyaryleneethynylenes incorporating electron-donor (OAlk) or electron acceptor (OCOAlk) substituents were synthesised¹²⁰⁻¹²² using the $\text{PdCl}_2\text{-Cu(OAc)}_2\text{-PPh}_3$ catalytic system in $\text{Et}_3\text{N-THF}$ solution. The use of THF, which is capable of solvating metal complexes (it is poor solubility of intermediate complexes that prevents formation of high-molecular-weight PARE¹²⁵) and the presence of alkyl substituents in the monomers provide a possibility to obtain polymers with molecular weights up to 100 000. The optical properties of these polymers are presented in Table 18.¹²¹

Oligomers (trimers and pentamers), which are better soluble than their high-molecular-weight analogues,¹²² form mesophases when heated. These oligomers are used in preparation of oriented materials for optoelectronics. The oligomers with short side chains show the best non-linear optical properties.

Some studies were devoted to the synthesis of PARE based on monomers incorporating vinylene groups.^{126, 127} Such reactions

usually yield polyenynes. Conjugated polyenynes incorporating thiophene fragments were obtained by reaction of 3,4-didecyloxy-2,5-bis(2-bromoethynyl)thiophene with diethynylbenzenes **76a-c** in the presence of $\text{PdCl}_2(\text{PPh}_3)_2\text{-CuI}$ in $\text{Et}_3\text{N-THF}$ mixture.¹²⁶



The properties of the thus synthesised polyenynes are presented in Table 19. Thin films were casted from solutions of these polymers.

Table 18. Optical properties of alkoxy- and alkoxy-carbonyl-substituted oligomers and corresponding polymers.¹²¹

Compound	$\lambda_{\max}$ in luminescence spectra /nm		$\nu_{\text{vis}}(\text{C}\equiv\text{C})$ in Raman spectra / cm^{-1}	$10^{10} \chi^{(3)}$ (DFWM, 620 nm) /cgs
	solution	film		
	376	378	2207	—
	378	383	—	2.5
	418	425	2200	3.6
	400	419	—	—
	344	337	—	—
	364	375	2204	—
	384	403	—	4.6

Initial compounds		$[\eta]^a$ /dl g ⁻¹	T_{exo} /°C	T_d^1 /°C	T_d^2 /°C
75a	76a	0.32	300	281	496
	76b	0.27	380	237	532
	76c	0.90	350	325	548
75a + 75b	76b	0.74	350	328	534

^a Measured in THF at 30 °C.

The catalytic system used was $\text{PdCl}_2[(\text{PTol-}p)_3]_2-(\text{PTol-}p)_3-\text{CuI}-\text{Et}_3\text{N}$. The synthesis was carried out in boiling dioxane for 24 h. All reactions proceeded homogeneously and yielded polymers soluble in THF, CHCl_3 and CH_2Cl_2 with relatively high molecular weight and narrow molecular weight distribution (polydispersity of 1.4–1.6) (Table 20).

Polymer	M_w	T_{exo}^a / $^{\circ}C$	$T_d(5\%)^b$ / $^{\circ}C$
78a	23000	190	240
78b	18000	183	250
78c	41000	175	340

^a Data of DSC. ^b Data of DTG.

were prepared^{129–132} by a reaction of 1,3,5-triethynylbenzene with 1,3,5-tribromobenzene or monomers of 1,3-diethynyl-5-bromobenzene type. Taking into account that the dendrite polymers are usually much better soluble than their linear analogues (when isolated before the gel point),^{132–134} one may predict that this approach in chemistry of PARV and PARE will find considerable development.

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